

RESEARCH ARTICLE

Computational Study of Metal Complexes and Their Interactions with Various Gas Molecules: Electronic Structure, Binding Mechanisms and Emerging Applications

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ABSTRACT

Metal complexes provide versatile and tunable platforms for molecular recognition and interaction with small gas molecules. Computational chemistry has become an important approach for understanding these interactions by revealing structural, energetic, and electronic changes that are often difficult to examine experimentally. Density functional theory and related quantum-chemical methods are widely applied to study gases such as CO, CO₂, NO, NO₂, NH₃, SO₂, H₂, O₂, N₂, and CH₄. Important computational descriptors include adsorption or binding energy, metal–gas distance, molecular geometry, charge transfer, frontier molecular orbitals, HOMO–LUMO energy gap, and electron-density-based analyses. These parameters help distinguish weak adsorption, coordination, and molecular activation mechanisms. Computational studies also support designing metal complexes for gas sensing, capture, separation, and catalytic applications. However, challenges remain in accurately treating transition-metal electronic structure, dispersion, realistic environmental conditions, selectivity, and adsorption–desorption balance. Future progress will require improved computational methods, experimental validation, and data-driven screening strategies.

Keywords: Metal complexes; Density functional theory; Gas adsorption; Gas sensing; Coordination chemistry; Electronic structure

FULL PAPER

1. Introduction

1.1 Importance of Gas Molecules

Small gas molecules play roles in environmental, industrial, biological, and energy processes. Carbon monoxide (CO), nitrogen dioxide (NO₂), and sulfur dioxide (SO₂) are atmospheric pollutants, and exposure may adversely affect health. Chen et al. (2022) reviewed epidemiological evidence and reported associations between exposure to these gases and respiratory or cardiovascular outcomes (Chen et al., 2022). Meanwhile, CO₂, H₂, O₂, N₂, and CH₄ support energy conversion, climate chemistry, combustion, and catalysis, while NH₃ and NO support industrial operations, biology, and environmental monitoring.

1.2 Metal Complexes as Gas-Interactive Molecular Systems

Metal complexes consist of a central metal ion or atom coordinated by surrounding ligands, and their behavior depends on both the metal and ligand environment. Melese et al. (2025) reviewed H₂, CO₂, and N₂ activation by transition-metal complexes and showed that metal identity, oxidation state, and coordination environment influence small-molecule binding and activation (Melese et al., 2025). Vacant coordination sites and tunable ligand donor properties further control gas accessibility and selectivity. Fielicke (2023) demonstrated that transition-metal systems provide useful models for understanding how small molecules bind and become activated at metal centers (Fielicke, 2023).

1.3 Need for Computational Investigation

Experimental studies can confirm gas binding, but they may not fully explain its molecular origin. Computational chemistry addresses this limitation by predicting optimized geometries, preferred binding sites, adsorption energies, charge redistribution, orbital changes, spin states, and reaction pathways. Nandy et al. (2021) noted that density functional theory is widely used for transition-metal complexes because it provides useful electronic-structure information at practical computational cost (Nandy et al., 2021). These calculations help explain differences in gas affinity and support interpretation of structural and spectroscopic observations.

1.4 Scope and Objective of the Review

This review examines computational studies of metal complexes interacting with different gas molecules, with particular emphasis on the structural and

electronic factors that govern binding strength, selectivity, and molecular activation. Jose et al. (2023) showed that molecular modelling can identify preferred gas-binding regions, estimate relative binding energies, and clarify the effects of metal ions, ligand environments, and spin states on adsorption behavior (Jose et al., 2023). The review therefore considers the major computational approaches used for these systems, the influence of metal and ligand characteristics, gas-specific interaction mechanisms, and the principal descriptors employed to interpret adsorption and electronic response. It also highlights applications in gas sensing, capture, separation, and catalytic activation, while identifying current methodological limitations and emerging research opportunities. Accordingly, the following sections progress from computational methods and structural–electronic factors to gas-specific studies and key descriptors, before discussing practical applications, current challenges, research gaps, and future perspectives.

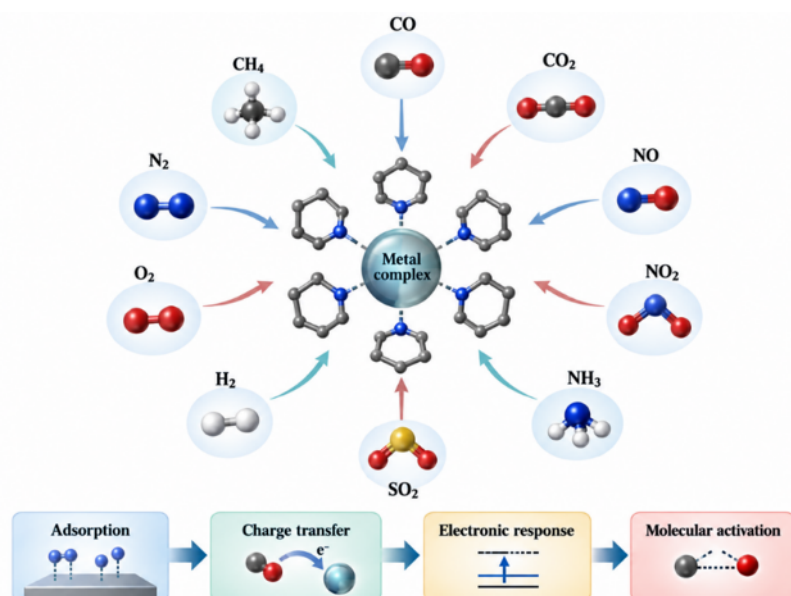


Figure 1. General representation of the interaction between a metal complex and different gas molecules.

2. Computational Approaches for Studying Metal Complex–Gas Interactions

2.1 Density Functional Theory

Density functional theory (DFT) is one of the most widely used quantum-chemical approaches for investigating metal complexes because it provides a practical balance between computational cost and accuracy. It is especially useful for transition-metal systems, where electronic structure, spin state, and metal–ligand interactions can strongly influence gas binding. Zhao and Truhlar (2008) evaluated the M06 family of functionals for a wide range of chemical problems,

including transition-metal chemistry and noncovalent interactions, demonstrating their usefulness for chemically diverse systems (Zhao & Truhlar, 2008). Depending on the system, commonly employed functionals include B3LYP, PBE, PBE0, M06, M06-2X, and ω B97X-D.

2.2 Basis Sets and Effective Core Potentials

The quality of a DFT calculation also depends on the basis set used to describe the electronic structure. Light atoms are commonly treated with basis sets such as 6-31G(d,p) and 6-311++G(d,p), whereas transition-metal systems often require more flexible basis sets. Weigend and Ahlrichs (2005) developed the def2 family, including def2-SVP and def2-TZVP, for broad application across the periodic table (Weigend & Ahlrichs, 2005). For heavier metals, effective core potentials such as LANL2DZ and SDD are frequently used to reduce computational cost while treating inner-core electrons effectively.

2.3 Dispersion Corrections

Weak gas–complex interactions may include an important dispersion contribution that conventional DFT does not always describe adequately. Grimme et al. (2010) introduced the DFT-D3 dispersion correction for a wide range of elements, providing a practical treatment of long-range dispersion forces (Grimme et al., 2010). Methods such as D3 and D3(BJ) are therefore useful for systems where physisorption contributes significantly to binding. Chai and Head-Gordon (2008) also developed the dispersion-inclusive ω B97X-D functional for improved treatment of noncovalent interactions (Chai & Head-Gordon, 2008).

2.4 Geometry Optimization and Frequency Analysis

A typical computational investigation begins by separately optimizing the isolated metal complex and the selected gas molecule. Several possible gas-binding orientations are then constructed and optimized to identify the most stable adduct. Frequency calculations are subsequently performed to confirm that the optimized structure corresponds to a true minimum on the potential-energy surface. A stable minimum is generally indicated by the absence of imaginary frequencies. These calculations can also provide information about structural distortion and vibrational changes associated with gas adsorption.

2.5 Adsorption and Interaction Energy

The energetic stability of a gas–complex adduct is commonly evaluated using adsorption energy:

$$E_{\text{ads}} = E_{\text{complex+gas}} - E_{\text{complex}} - E_{\text{gas}}$$

With this convention, a more negative adsorption energy generally indicates a more favorable interaction. However, adsorption energy, binding energy, and interaction energy are not always defined identically across studies, so consider the convention used by each author. Basis-set superposition error can artificially strengthen calculated intermolecular interactions. Boys and Bernardi (1970) introduced the counterpoise correction method, which remains widely used to estimate and reduce this error (Boys & Bernardi, 1970).

2.6 Solvent, Temperature and Environmental Effects

Gas-phase calculations describe intrinsic metal–gas interactions, but experimental systems may operate under more complex conditions. Implicit solvent models can estimate solvent effects, while thermal and Gibbs-energy corrections provide information beyond electronic energies alone. Temperature, pressure, humidity, solvent, and competing gas molecules may therefore influence binding strength, selectivity, and desorption behavior.

2.7 Computational Software

Several established quantum-chemical and electronic-structure packages are available for studying metal complex–gas interactions. Commonly used programs include Gaussian, ORCA, GAMESS, VASP, and Quantum ESPRESSO. The choice of software generally depends on whether the system is molecular or periodic, the required level of theory, and the type of electronic analysis to be performed.

Table 1. Common computational approaches used for investigating metal complex–gas interactions

Computational aspect	Common approaches	Information obtained
Geometry optimization	DFT	Stable molecular structure and preferred adsorption geometry
Exchange–correlation treatment	B3LYP, PBE, PBE0, M06, M06-2X, ω B97X-D	Electronic structure and energetic properties

Basis sets	6-31G(d,p), 6-311++G(d,p), def2-SVP, def2-TZVP, LANL2DZ, SDD	Representation of molecular orbitals and electron distribution
Dispersion treatment	D3, D3(BJ), ω B97X-D	Weak intermolecular and van der Waals interactions
Frequency calculation	Harmonic vibrational analysis	Confirmation of structural stability and vibrational properties
Charge analysis	NPA, Hirshfeld, Mulliken	Electron redistribution and charge transfer
Bond analysis	NBO, QTAIM, NCI/RDG	Nature and strength of intermolecular interactions
Excited-state analysis	TD-DFT	Optical and electronic excitation behavior

3. Structural and Electronic Features Governing Gas Interaction

3.1 Nature of the Central Metal Ion

The central metal ion strongly determines how a complex interacts with a gas molecule. Important factors include metal identity, ionic radius, oxidation state, d-electron configuration, Lewis acidity, spin state, and the presence of an open coordination site. Mandal et al. (2014) compared Ni^{2+} , Cu^{2+} , and Zn^{2+} complexes and showed that changing the metal ion alters coordination behavior and the electronic structure of the resulting complex (Mandal et al., 2014). Such differences influence orbital availability and electron density at the metal center. Consequently, replacing one transition metal with another can substantially modify gas-binding strength, orientation, and charge-transfer behavior.

3.2 Effect of Ligand Environment

The ligand framework regulates the electronic and steric environment around the metal center. Electron-donating ligands can increase electron density on the metal, whereas electron-withdrawing groups may produce the opposite effect. Ligand rigidity, conjugation, donor atoms, and steric crowding also control

accessibility of potential gas-binding sites. Cavigliasso et al. (2008) computationally examined a series of Co(III) complexes containing different tripodal tetraamine ligands and found that changes in ligand identity and size influenced Co–N bonding and related structural and spectroscopic properties (Cavigliasso et al., 2008). Similar ligand-dependent tuning is possible in Schiff-base, salen, porphyrin, phthalocyanine, macrocyclic, and organometallic complexes, making ligand design an important route for controlling gas affinity.

3.3 Coordination Geometry

Coordination geometry determines both the spatial arrangement of ligands and the metal center's accessibility. Tetrahedral, square-planar, octahedral, square-pyramidal, and trigonal-bipyramidal environments provide different steric and electronic conditions for gas-molecule approach. Mandal et al. (2015) showed through experimental and quantum-chemical analysis that coordination of first-row transition-metal ions with L-serine produced metal-dependent structural and electronic changes (Mandal et al., 2015). In gas-binding systems, coordinatively unsaturated geometries or complexes containing an accessible axial site are generally more favorable for direct metal–gas interaction.

3.4 Spin State and Electronic Configuration

Spin state is particularly important for open-shell transition-metal complexes because high-spin and low-spin configurations differ in d-orbital occupancy and therefore in their ability to interact with adsorbates. Swart and Gruden (2016) emphasized that transition-metal complexes can have several energetically accessible spin states, and that their relative stability depends on both the metal and its surrounding ligand field (Swart & Gruden, 2016). Gas binding can alter ligand-field splitting and may therefore modify the preferred spin state. Cunningham et al. (2017), in their study of Cu, Ag, and Au complexes with N₂O, demonstrated that metal identity influences binding orientation, structural isomerism, and calculated ligand-binding energies (Cunningham et al., 2017). Spin and electronic configuration are especially relevant for interactions involving open-shell gases such as O₂, NO, and NO₂.

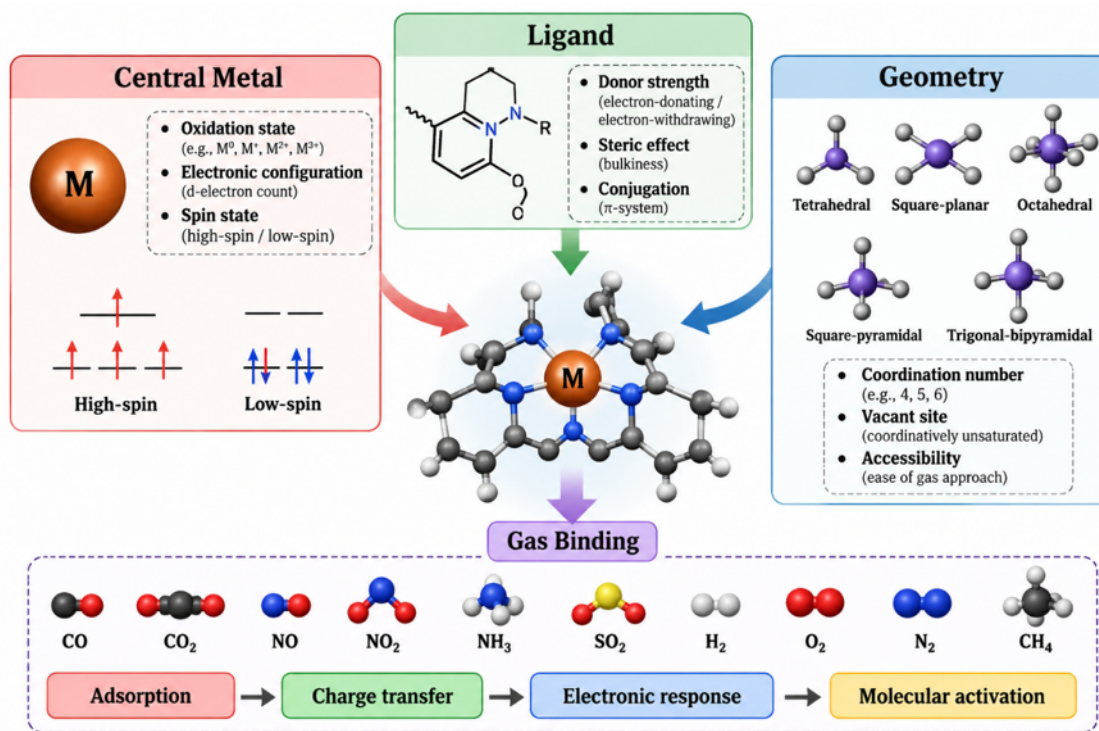


Figure 2. Major structural factors controlling gas binding in metal complexes.

4. Computational Studies of Metal Complex Interactions with Various Gas Molecules

4.1 Carbon Monoxide Interaction

Carbon monoxide interacts strongly with many transition-metal complexes through a combination of σ donation from CO to the metal and π back-donation from occupied metal d orbitals to the antibonding orbitals of CO. Ammar and Badran (2019) computationally studied CO adsorption on transition-metal porphyrins and showed that the central metal strongly influenced adsorption strength, charge redistribution, and electronic properties (Ammar & Badran, 2019). Stronger back-donation can weaken the C–O bond, modify the M–C distance, and produce characteristic vibrational-frequency shifts. These changes make CO a useful probe for understanding metal–ligand electronic interactions.

4.2 Carbon Dioxide Interaction

CO₂ is normally linear and relatively stable, but interaction with an electron-rich metal center can induce C–O bond bending and elongation. Uddin et al. (2024) screened a series of metalloporphyrins and evaluated CO₂ activation using binding

energy, molecular distortion, and charge-transfer parameters (Uddin et al., 2024). Their study showed that metal identity, oxidation state, and ligand substitution strongly influence CO₂ activation. Depending on the complex, CO₂ may interact through carbon- or oxygen-centered configurations. Such computational studies help identify metal complexes suitable for CO₂ capture and catalytic conversion.

4.3 Nitric Oxide Interaction

NO is an open-shell radical, and its coordination with transition metals is strongly affected by metal oxidation state and spin configuration. Zhao et al. (2018) investigated NO adsorption on several metal-phthalocyanine systems and reported noticeable changes in magnetic and electronic properties following gas binding (Zhao et al., 2018). Metal–NO bonding may involve both electron donation from NO and back-donation from metal orbitals. Depending on these interactions, linear or bent coordination geometries may be favored.

4.4 Nitrogen Dioxide Interaction

NO₂ is a strong electron acceptor and can therefore produce significant charge transfer when coordinated to suitable metal centers. Zhao et al. (2018) showed that NO₂ adsorption on metal-phthalocyanine systems could alter electronic transport and magnetic behavior (Zhao et al., 2018). Both N-bound and O-bound geometries are possible, depending on the metal and ligand environment. Changes in molecular orbitals and conductivity after adsorption make these complexes attractive candidates for computational design of NO₂ sensors.

4.5 Ammonia Interaction

NH₃ generally binds through donation of its nitrogen lone pair to an electron-deficient metal center. Badran et al. (2024) investigated NH₃ adsorption on manganese phthalocyanine and found noticeable charge redistribution and changes in the HOMO–LUMO energy gap after adsorption (Badran et al., 2024). The interaction therefore has a strong Lewis acid–base character and may lead to formation of an M–N coordination bond. Such electronic changes are useful indicators for predicting the gas-sensing response of metal complexes.

4.6 Sulfur Dioxide Interaction

SO₂ is a polar molecule that may interact with metal centers through either sulfur or oxygen atoms. Computational studies generally show that the preferred orientation depends on the metal center, charge distribution, and coordination-site accessibility. Fielicke (2023) reviewed small-molecule binding to transition-metal systems and emphasized that metal identity and electronic structure strongly

control adsorption geometry and bond activation(Fielicke, 2023). For SO₂, strong charge redistribution and molecular distortion can enhance its detection or capture.

4.7 Hydrogen Interaction

H₂ may interact weakly through van der Waals forces or more strongly through a Kubas-type interaction. In the latter case, σ donation from H₂ to the metal is accompanied by metal-to-H₂ back-donation into the σ^* orbital. Fielicke (2023) discussed how transition-metal centers can promote such small-molecule activation through orbital interactions (Fielicke, 2023). Partial population of the H₂ antibonding orbital weakens the H–H bond and is particularly relevant to reversible hydrogen-storage systems.

4.8 Oxygen Interaction

O₂ has a triplet ground state, making spin particularly important in its interaction with transition-metal complexes. Electron transfer from a metal center to O₂ can produce superoxo- or peroxo-like species and weaken the O–O bond. Fielicke (2023) highlighted the importance of metal electronic configuration and spin state in determining small-molecule activation at transition-metal centers (Fielicke, 2023). Such processes are central to oxidation catalysis and oxygen-transfer chemistry.

4.9 Nitrogen and Methane Interaction

N₂ is difficult to activate because of its strong N $\equiv$ N triple bond. Successful coordination generally involves σ donation from N₂ together with metal-to-N₂ π back-donation, which weakens the triple bond. CH₄ is similarly difficult to activate because of its low polarity and strong C–H bonds. Fielicke (2023) showed that small-molecule activation at transition-metal centers depends strongly on orbital availability, metal electronic configuration, and coordination environment (Fielicke, 2023). Computational studies therefore help identify metal systems that promote N₂ activation or initial C–H bond weakening in methane.

5. Computational Descriptors for Characterizing Gas–Complex Interactions

5.1 Adsorption and Binding Energy

Adsorption or binding energy is a descriptor for evaluating the strength and favorability of gas–complex interactions. Jose et al. (2023) emphasized calculated binding energies for comparing adsorption sites and gas affinities in metal-containing systems (Jose et al., 2023). Weakly favorable values usually indicate physisorption, whereas stronger stabilization may suggest coordination or

chemisorption. Because energy scales depend on the method, system, and sign convention, avoid universal numerical limits.

5.2 Structural Parameters

Structural changes reveal how gas binding perturbs a complex. Descriptors include metal–gas distance, intramolecular bond lengths, bond angles, coordination geometry, and molecular distortion. Gas-induced elongation, bending, or reorientation may indicate activation and should be interpreted together with energetic results (Jose et al., 2023).

5.3 Frontier Molecular Orbital Analysis

Frontier molecular orbitals are widely used to evaluate electronic response after adsorption. Nandy et al. (2021) identified HOMO and LUMO energies as useful DFT-derived descriptors for transition-metal complexes (Nandy et al., 2021). The energy gap is

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$$

Gas adsorption can shift these orbital energies and alter the gap, indicating changes in reactivity, electron-transfer tendency, and sensing behavior.

5.4 Charge-Transfer Analysis

Charge analysis identifies whether the gas behaves mainly as an electron donor or acceptor. Mulliken, natural population analysis, Hirshfeld, CM5, and Bader approaches can quantify electron redistribution, although values remain method-dependent. Comparing isolated fragments with the optimized adduct reveals the direction and approximate magnitude of charge transfer (Puzzarini et al., 2020).

5.5 Molecular Electrostatic Potential

Molecular electrostatic potential maps visualize electron-rich and electron-deficient regions and can suggest preferred gas-binding sites. They help locate nucleophilic and electrophilic regions before optimization and interpret electrostatic contributions to adsorption.

5.6 NBO Analysis

Natural bond orbital analysis converts electronic-structure results into chemically intuitive donor–acceptor interactions. Weinhold and Landis (2016) described its usefulness for examining orbital delocalization, charge transfer, and donor–acceptor stabilization (Weinhold & Landis, 2016). For gas complexes, NBO analysis can identify gas-to-metal donation or metal-to-gas back-donation and estimate stabilization energies.

5.7 QTAIM and NCI/RDG Analyses

Electron-density approaches provide insight into gas binding. Puzzarini et al. (2020) emphasized combining theoretical descriptors with experiment when characterizing noncovalent interactions (Puzzarini et al., 2020). QTAIM examines topological electron-density features, while NCI/RDG analysis visualizes weak attractive and repulsive regions, helping distinguish covalent, ionic, hydrogen-bonding, and van der Waals contributions.

5.8 DOS/PDOS and Spectroscopic Parameters

DOS and PDOS analyses identify metal, ligand, and gas contributions to important electronic states. Alvand et al. (2026) combined DFT, TD-DFT, and reduced-density-gradient analysis to relate adsorption with electronic and optical changes (Alvand et al., 2026). Calculated IR shifts, UV–Vis changes, and TD-DFT transitions can further connect predicted gas binding with experimentally measurable responses.

6. Applications of Metal Complex–Gas Interactions

6.1 Gas Sensing

Metal complex–gas interactions have important applications in sensing because gas binding can alter a complex's electronic structure. Sax et al. (2009) discussed transition-metal-based optical oxygen sensors in which oxygen concentration is detected through changes in luminescence behavior (Sax et al., 2009). In computational sensor design, sensitivity and selectivity are assessed from adsorption strength, electronic response, conductivity-related changes, and shifts in the HOMO–LUMO gap. Reversible binding is also important because excessively strong adsorption can hinder desorption, whereas moderate interaction can support repeated sensing and recovery cycles.

6.2 Gas Capture and Separation

Gas capture and separation depend on selective, reversible interactions between a gas molecule and a metal-containing host. Ramprasad et al. (1993) described cobalt- and iron-based oxygen absorbents capable of reversible oxygen uptake for non-cryogenic air separation (Ramprasad et al., 1993). Bakhshian and Sahimi (2018) modeled adsorption and structural deformation in flexible metal–organic frameworks, showing that framework response can influence gas uptake (Bakhshian & Sahimi, 2018). Similar principles apply to CO₂ and SO₂ capture, toxic-gas removal, and selective adsorption.

6.3 Catalytic Activation of Small Molecules

Computational chemistry is important for understanding small-molecule activation. Johnson (2009) related electronic structure and electronegativity concepts to transition-metal reactivity, providing a basis for interpreting gas activation at metal centers (Johnson, 2009). First-principles simulations can clarify bond weakening, electron transfer, and reaction pathways involving CO₂, O₂, N₂, H₂, and CH₄. Brunk et al. (2011) emphasized the growing role of first-principles simulations in complex chemical systems (Brunk et al., 2011). Such predictions help identify intermediates, compare pathways, and guide catalyst design.

6.4 Environmental and Industrial Monitoring

Metal complex–gas interactions are also relevant to environmental and industrial monitoring. Selective binding and measurable electronic or optical responses can support detection of CO, NO_x, SO₂, NH₃, oxygen, and greenhouse gases. The sensing and adsorption principles described for transition-metal complexes and flexible metal-containing materials (Johnson, 2009; Brunk et al., 2011; Tolbatov et al., 2022) show how molecular recognition can be translated into monitoring platforms for air-quality assessment, process control, and safety.

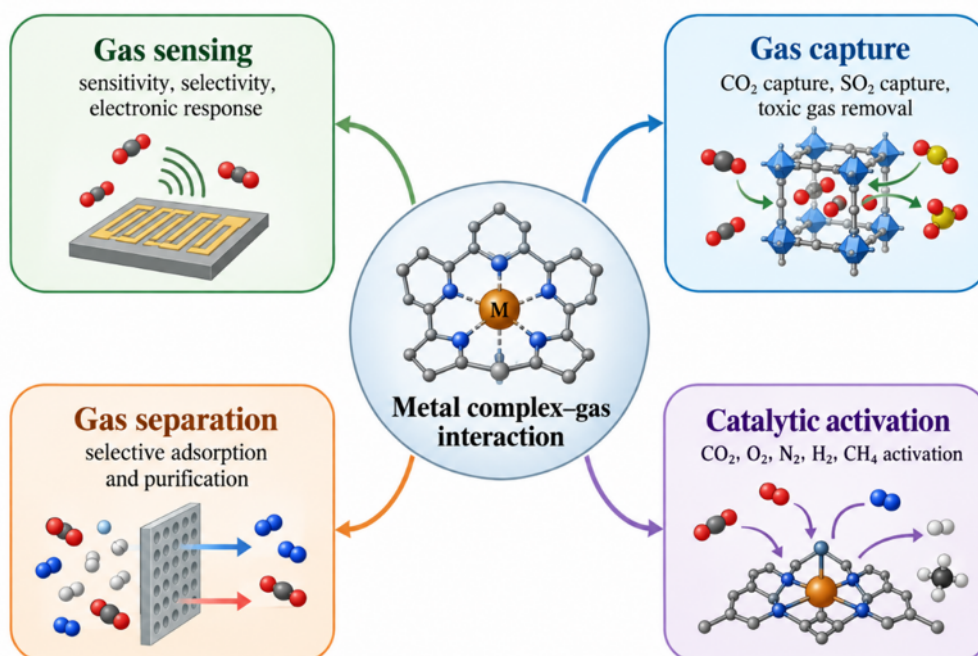


Figure 3. Potential applications of computationally designed metal complexes for gas interaction.

7. Current Challenges, Research Gaps and Future Perspectives

7.1 Method-Dependent Results

Computational predictions of gas–complex interactions depend strongly on the selected functional, basis set, dispersion treatment, and solvation model. Tolbatov et al. (2022) emphasized that different computational strategies can produce noticeable variations in structures, energetics, and reactivity predictions for transition-metal complexes (Tolbatov et al., 2022). Careful methodological validation is therefore essential.

7.2 Treatment of Transition Metals

Transition-metal systems remain difficult because multiple spin states, strong electron correlation, relativistic effects, and multireference character may influence calculated properties. Vogiatzis et al. (2019) highlighted these challenges in computational studies of 3d-metal catalysis and stressed the need for methods that can treat electronically complex systems reliably (Vogiatzis et al., 2019).

7.3 Realistic Experimental Conditions

Many calculations are still performed in vacuum, at idealized temperatures, and with only one gas molecule. Future models should better represent temperature, pressure, humidity, solvent effects, and competing gases. Yang et al. (2013) showed that realistic modeling conditions are important when computational methods are applied to gas adsorption and separation in metal-containing frameworks (Yang et al., 2013).

7.4 Selectivity toward Competing Gases

Strong adsorption alone does not establish selectivity. Mohan (2025) emphasized that noncovalent interactions can control recognition and sensing behavior in metal-coordinated complexes (Mohan, 2025). Comparative calculations involving several gases are therefore needed to determine whether a complex preferentially binds the target molecule.

7.5 Adsorption–Desorption Balance

An effective gas-binding material should balance adsorption and desorption. Weak binding may produce limited sensitivity, whereas very strong chemisorption can hinder recovery and regeneration. Computational screening should therefore identify systems with interaction strengths suitable for both detection and reversible release.

7.6 High-Throughput Computational Screening

High-throughput computational screening can reduce the current reliance on isolated metal–ligand–gas combinations by systematically evaluating a large metal $\times$ ligand $\times$ gas chemical space. For example, a virtual library could be generated using 10 transition metals, 10 ligand frameworks, and 8 target gases, producing 800 candidate systems. Each system could first be screened using a lower-cost DFT protocol for adsorption energy, metal–gas distance, charge transfer, and HOMO–LUMO gap change. The most promising candidates could then be re-evaluated using higher-level calculations, dispersion corrections, solvent effects, and competing gases. This stepwise approach would help identify metal–ligand combinations that provide not only strong adsorption but also selectivity and suitable desorption behavior, thereby addressing current gaps in comparative screening and rational gas-sensor or catalyst design.

8. Conclusions

Metal complexes provide highly tunable chemical environments for interacting with a wide range of gas molecules. Their adsorption behavior is controlled jointly by the identity and electronic state of the central metal, the ligand framework, coordination geometry, and availability of binding sites. Density functional theory has become a valuable tool for understanding these interactions at the molecular level. Adsorption energy, optimized geometry, charge transfer, frontier molecular orbitals, and related electronic descriptors are commonly used to evaluate gas binding and activation. Different gases exhibit distinct interaction mechanisms, ranging from weak physisorption to strong coordination and bond activation. Computational screening can therefore support the design of improved gas sensors, capture materials, separation systems, and catalysts. Future progress will depend on combining accurate calculations with realistic conditions, experimental validation, and data-driven approaches.

References

- Alvand, R., Rezaei-Sameti, M., Rajaie Khorasani, R., & Gharib, M. (2026). Computational study of pristine, Al- and P-doped B₁₂N₁₂ nanocages for BrCN adsorption and detection under electrostatic fields using density functional theory, time-dependent density functional theory, and reduced density gradient. *ChemPhysChem*.

- Ammar, H. Y., & Badran, H. M. (2019). Effect of CO adsorption on properties of transition metal doped porphyrin: A DFT and TD-DFT study. *Heliyon*, 5(10), e02545.
- Badran, H. M., Eid, K. M., Al-Nadary, H. O., & Ammar, H. Y. (2024). DFT-D3 and TD-DFT studies of the adsorption and sensing behavior of Mn-phthalocyanine toward NH₃, PH₃, and AsH₃ molecules. *Molecules*, 29(10), 2168.
- Bakhshian, S., & Sahimi, M. (2018). Theoretical model and numerical simulation of adsorption and deformation in flexible metal–organic frameworks. *The Journal of Physical Chemistry C*.
- Boys, S. F., & Bernardi, F. (1970). The calculation of small molecular interactions by the differences of separate total energies: Some procedures with reduced errors. *Molecular Physics*, 19(4), 553–566.
- Brunk, E., Ashari, N., Athri, P., Campomanes, P., et al. (2011). Pushing the frontiers of first-principles based computer simulations of chemical and biological systems. *CHIMIA*.
- Cavigliasso, G., Stranger, R., McClintock, L. F., Cheyne, S. E., Jaffray, P. M., Baxter, K. E., & Blackman, A. G. (2008). A computational study of the electronic structure, bonding, and spectral properties of tripodal tetraamine Co(III) carbonate complexes. *Dalton Transactions*, 2433–2444.
- Chai, J.-D., & Head-Gordon, M. (2008). Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Physical Chemistry Chemical Physics*, 10, 6615–6620.
- Chen, Z., Liu, N., Tang, H., Gao, X., et al. (2022). Health effects of exposure to sulfur dioxide, nitrogen dioxide, ozone, and carbon monoxide between 1980 and 2019: A systematic review and meta-analysis. *Indoor Air*, 32(11), e13170.
- Cunningham, E. M., Gentleman, A. S., Beardsmore, P. W., Iskra, A., & Mackenzie, S. R. (2017). Infrared signature of structural isomers of gas-phase M⁺(N₂O)_n (M = Cu, Ag, Au) ion–molecule complexes. *The Journal of Physical Chemistry A*, 121(40), 7565–7571.
- Fielicke, A. (2023). Probing the binding and activation of small molecules by gas-phase transition metal clusters via IR spectroscopy. *Chemical Society Reviews*, 52, 3778–3841.

- Grimme, S., Antony, J., Ehrlich, S., & Krieg, H. (2010). A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *The Journal of Chemical Physics*, 132, 154104.
- Johnson, K. H. (2009). Spin-orbital electronegativity, the X α method, and reactivity at transition-metal interfaces. *International Journal of Quantum Chemistry*.
- Jose, R., Bangar, G., Pal, S., & Rajaraman, G. (2023). Role of molecular modelling in the development of metal-organic framework for gas adsorption applications. *Journal of Chemical Sciences*, 135, 19.
- Mandal, S., Das, G., & Askari, H. (2014). Interactions of N-acetyl-L-cysteine with metals (Ni²⁺, Cu²⁺ and Zn²⁺): An experimental and theoretical study. *Structural Chemistry*, 25, 543–556.
- Mandal, S., Das, G., & Askari, H. (2015). A combined experimental and quantum mechanical investigation on some selected metal complexes of L-serine with first row transition metal cations. *Journal of Molecular Structure*, 1081, 281–292.
- Melese, A., Wubet, W., Hussen, A., Temesgen, A., & Mulate, K. (2025). Review on activation of small molecules (dihydrogen, carbon dioxide, and dinitrogen) by various transition metal complexes. *Journal of Chemical Research*.
- Mohan, B. (2025). Understanding the role of noncovalent interactions in gas sensing with metal-coordinated complexes (MCCs). *Topics in Current Chemistry*.
- Nandy, A., Duan, C., Taylor, M. G., Liu, F., Steeves, A. H., & Kulik, H. J. (2021). Computational discovery of transition-metal complexes: From high-throughput screening to machine learning. *Chemical Reviews*, 121(16), 9927–10000.
- Puzzarini, C., Spada, L., Alessandrini, S., & Barone, V. (2020). The challenge of non-covalent interactions: Theory meets experiment for reconciling accuracy and interpretation. *Journal of Physics: Condensed Matter*, 32, 343002.
- Ramprasad, D., Gilicinski, A. G., Markley, T. J., & Pez, G. P. (1993). New metal complex oxygen absorbents for the recovery of oxygen. *ChemInform*.
- Sax, S., Neuhold, A., & List, E. J. W. (2009). Novel concepts for organic optical oxygen sensor devices.
- Swart, M., & Gruden, M. (2016). Spinning around in transition-metal chemistry. *Accounts of Chemical Research*, 49(12), 2690–2697.
-

- Tolbatov, I., et al. (2022). Computational strategies to model the interaction and the reactivity of biologically-relevant transition metal complexes. *Inorganica Chimica Acta*.
- Uddin, A. T., Zhao, Q., Toroz, D., Crespo-Otero, R., & Di Tommaso, D. (2024). Computational screening of metalloporphyrin catalysts for the activation of carbon dioxide. *Molecular Catalysis*, 565, 114386.
- Vogiatzis, K. D., et al. (2019). Computational approach to molecular catalysis by 3d transition metals: Challenges and opportunities. *Chemical Reviews*.
- Weigend, F., & Ahlrichs, R. (2005). Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Physical Chemistry Chemical Physics*, 7, 3297–3305.
- Weinhold, F., & Landis, C. R. (2016). What is NBO analysis and how is it useful? *International Reviews in Physical Chemistry*, 35(3), 399–440.
- Yang, Q., et al. (2013). Development of computational methodologies for metal–organic frameworks and their application in gas separations. *Chemical Reviews*.
- Zhao, W., Zou, D., Sun, Z., Yu, Y., et al. (2018). Controlling spin off state by gas molecules adsorption on metal-phthalocyanine molecular junctions and its possibility of gas sensor. *Physics Letters A*, 382(37), 2666–2672.
- Zhao, Y., & Truhlar, D. G. (2008). The M06 suite of density functionals for main-group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts*, 120, 215–241.