nature portfolio

Peer Review File

Framework-Templated Gas Lattices in Metal-Organic Frameworks

Corresponding Author: Professor Jihan Kim

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript presents a workflow for designing framework-templated gas lattices in MOFs, together with a screening strategy and the construction and optimization of a series of pillared MOFs to enable targeted control of gas-lattice formation. The study advances high-performance MOF design from a conventional material-guided paradigm toward an adsorbate-phase design concept, providing valuable insights for the development of novel gas separation materials. I would consider recommending this manuscript for publication after the authors adequately address the following issues.
1. The practical implications of gas-lattice formation remain somewhat underexplored. It is not yet fully clear whether such ordering leads to improved adsorption, or separation performance compared with existing MOFs.
2. The phenomenon is mainly demonstrated for xenon. Can the authors comment on whether this concept can be generalized to other gas systems?
3. The neighbor-count descriptor is used as a key metric throughout the study. Is it sufficient to reliably characterize gas-lattice formation and material performance?
4. The simulations rely on the UFF force field. Could the authors comment on its suitability and limitations for describing gas behavior in these systems?
5. Are the inverse-designed structures potentially experimentally synthesizable?
6. Could the authors more clearly compare the proposed adsorbate-phase design concept with conventional performance-guided MOF design strategies?

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)
The authors introduce the concept of framework-templated gas lattices to describe structurally defined adsorption states in metal-organic frameworks (MOFs), identifying Co-CAU-36 as a host for a pore-spanning Xenon lattice through high-throughput screening. A key motivation of this work is to move beyond traditional adsorbent-focused design by targeting the adsorbed phase itself to better understand uptake and transport.

While the proposed "lattice gas" concept offers an interesting perspective for modeling adsorption behaviors in nanoporous materials, the observed phenomenon is highly constrained to very specific temperatures, a single gas species, and strict framework conditions. Based on the manuscript, the applicability of this concept to other varying systems or broader operating conditions appears extremely limited. Furthermore, the calculated lattice constants exhibit a strong dependency on the selected empirical force fields. Although the authors attempt to supplement their study with additional density functional theory (DFT) calculations, this underlying force-field sensitivity raises reasonable doubts regarding the physical realism and robustness of the lattice gas phenomenon in practical environments.

Ultimately, given the highly conditional nature and narrow applicability of these findings, the manuscript does not align with the broad interest and general audience scope required by Nature Communications. While the study offers useful insights into a highly specific system, this after-the-fact approach under restricted conditions makes the work much more appropriate for a specialized journal in physical chemistry or materials science. Therefore, I recommend rejection.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)
In this work the authors demonstrate that Xe which normally condenses to an FCC fluid can create BCC structures in certain MOFs due to ideal pore size/shape. They also implement a framework for identifying or designing MOFs with the proper structures to achieve this effect. It is an interesting fundamental study combining adsorption and crystallization thermodynamics. I think it needs to be shown a bit more rigorously that this is not a box size effect by doing a convergence test with the simulation box size. I offer some further comments below. I think it should be published with a few edits

Fig 1: I take some issue with labeling adsorbate interactions as ‘weak” in the left side of figure 1. Polar molecules like water and alcohol can have very strong interactions in a MOF. Similarly I don’t think interactions between the chosen exemplar of Xenon are going to be that strong even when adsorbed to a lattice. Really this is more of an entropic effect than about strength of adsorbate-adsorbate interactions

P 11, line 189: it seems the confinement may force the Xe into a BCC lattice which is unusual for a LJ fluid. I think it needs to be checked rigorously this is a real effect and not the result of some finite size artifact. Does the same thing happen if the simulation box is increased?
Did the authors consider HCP lattices which would generally be more favored over BCC for an LJ fluid?

I think there needs to generally be more discussion about the effects of entropy in this system which is very important for this kind of ordering

It might help to frame this discussion in terms of the lattice constant of FCC/BCC xenon and compare that to the MOF lattice constant. Is this effect more nuanced than the MOF lattice constant aligning with a multiple of BCC Xe causing BCC to be favored?

Could the authors offer some comment about how more complicated – non spherical – adsorbates would behave?

(Remarks on code availability)
I had trouble loading the files from github. Authors should check this is working. It might just be a temporary server issue

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have addressed my concerns, and I have no further major objections to publication. While the conceptual contribution is clear, the manuscript would benefit from a more explicit discussion of how this phenomenon translates to practical performance metrics. A minor suggestion is to further clarify the description of the structural analysis (e.g., NC metric and validation) for better readability. Additionally, a brief discussion on the implications for adsorption or separation performance would further strengthen the practical context.

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)
I would like to thank the authors for their detailed responses. Thanks to the in-depth revisions, the manuscript has significantly improved. However, before it can be considered fully suitable for publication, a couple of critical points regarding the validation of the simulation methodology must be addressed more rigorously.

1. The fundamental question regarding whether the observed "crystal formation" is merely a force field (FF) artifact hinges on whether UFF can accurately simulate adsorption behavior and absolute adsorption capacities under cryogenic conditions, specifically at 100 K. Unless the accuracy of UFF in modeling absolute adsorption at 100 K is rigorously validated, it is difficult to accept the findings as a realistic physical phenomenon. Although Supplementary Figure 2 demonstrates that UFF meaningfully captures the trend of adsorption in HKUST-1 at 280 K and shows some correlation with experimental Xe/Kr selectivity, this does not guarantee that UFF will reliably simulate adsorption behavior at 100 K.
Furthermore, regarding the comparison results for HKUST-1, it must be clarified: what were the isotherms normalized against? While demonstrating the validity of UFF through the similarity of normalized isotherms might be acceptable in some contexts, it is inadequate here. Because crystal formation is strictly governed by the absolute amount of adsorption, the simulated adsorption capacity must match experimental values at the specific temperature and pressure of interest. The

primary point of comparison should be at 100 K, where crystal formation is most clearly observed. The authors are required to demonstrate that UFF can reproduce experimental adsorption capacities and behavior at such low temperatures. The reliability of the crystal formation—which is the central point of this manuscript—cannot be adequately justified merely by showing a general correlation in adsorption capacity and selectivity under standard conditions.

2. The authors argued that crystal formation is also observed when using the Dreiding force field, presenting this as evidence that it is not a FF artifact. However, as shown in Supplementary Figure 4, the pressure-dependent trends differ significantly between the force fields even at the same temperature. Rather than resolving the issue, this actually highlights the strong dependence of the results on the chosen force field. In other words, even if the phenomenon is computationally possible, the fact that the specific thermodynamic conditions (temperature and pressure) required for crystal formation vary heavily depending on the FF leaves the physical reality of the phenomenon in question. While I agree with the authors that this work holds value as a "proof of concept," the doubts regarding its actual physical manifestation remain unresolved. To fully address this, the authors need to provide validation through alternative, higher-accuracy simulation methodologies (e.g., ab initio or higher-tier computational methods) or direct experimental evidence.

3. Based on the results presented in Supplementary Figure 6, the authors argue that crystal formation is not exclusive to 100 K but can also occur at other temperatures including 300 K. However, to convincingly demonstrate that the filling of molecules near the surface at 300 K truly represents the onset of lattice formation, the authors need to provide evidence at higher pressures. Specifically, it is necessary to show that as the pressure increases further—leading to a higher total adsorption capacity—a well-defined crystal structure actually forms at 300 K, identical to the behavior observed at 100 K.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)
The authors have addressed all my concerns fairly thoroughly. I think the manuscript is suitable for publication in its current form

(Remarks on code availability)
I was able to access the code this time.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
My queries have been satisfactorily addressed by the authors in the revised manuscript.

(Remarks on code availability)

In this point-by-point response to Reviewers' comments

1. **Black color** – comments from the Reviewers
2. **Blue color** – response to the comments
3. **Green color** – added in the manuscript with page number provided

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Reviewer #1 (Remarks to the Author):

This manuscript presents a workflow for designing framework-templated gas lattices in MOFs, together with a screening strategy and the construction and optimization of a series of pillared MOFs to enable targeted control of gas-lattice formation. The study advances high-performance MOF design from a conventional material-guided paradigm toward an adsorbate-phase design concept, providing valuable insights for the development of novel gas separation materials. I would consider recommending this manuscript for publication after the authors adequately address the following issues.

We sincerely appreciate the reviewer for their thoughtful summary and recognition of the novelty and systematic approach of our work. We are grateful for the acknowledgment that this study suggests a paradigm shift from the conventional material-guided design toward the adsorbate-phase design.

We are encouraged by the reviewer's support and have carefully addressed all suggestions to further improve the clarity, consistency, and scope of the manuscript.

1. The practical implications of gas-lattice formation remain somewhat underexplored. It is not yet fully clear whether such ordering leads to improved adsorption, or separation performance compared with existing MOFs.

We thank the reviewer for this important comment. We agree that the original manuscript did not sufficiently distinguish between two different questions: 1) whether framework-templated gas-lattice formation constitutes a structurally distinct and designable adsorbed phase, and 2) whether such gas-lattice formation necessarily translates into universally superior adsorption or separation performance relative to existing benchmark MOFs. In the revised manuscript, we have

clarified that the primary contribution of this work is the former, while the latter is presented more cautiously as a mechanistically motivated opportunity rather than a universal performance claim.

Specifically, we have revised the text to make clear that our central advance is the introduction of an adsorbate-phase design framework, in which the adsorbed phase itself is treated as an explicit design target, rather than the assertion that gas-lattice-forming MOFs are always superior performers in conventional screening metrics. As now stated more explicitly, the practical significance of gas-lattice formation lies in its ability to generate structure-defined, cooperative adsorption states that can influence how uptake is distributed across pressure, how pore filling reorganizes at high loading, and how mixed-gas adsorption can produce spatially differentiated motifs such as the Xenon-rich shell and Krypton-rich core arrangement observed in Co-CAU-36.

To address the reviewer's concern more directly, we have expanded the discussion of practical implications in two ways. First, we now emphasize that gas-lattice formation is not expected to guarantee higher uptake in every case. Rather, its value is that it provides a route to more controllable adsorption thermodynamics and spatial organization within the pore. This suggests that gas lattice formation may help concentrate working capacity into a relatively narrow operating window and may offer a useful handle for applications that benefit from cooperative or switching-like adsorption responses.

Pg 14

"…Importantly, we do not suggest that framework-templated gas-lattice formation necessarily yields the highest adsorption capacity relative to existing MOFs in all cases. Rather, its significance lies in enabling more controllable adsorption thermodynamics and spatial organization within the pore. This behavior suggests that adsorbate-phase design could help concentrate working capacity into a user-defined operating window and provide a potentially useful handle for gas capture applications that benefit from sharp uptake steps and controllable switching-like adsorption responses."

Second, we have clarified that the binary Xenon/Krypton results should be interpreted as a proof-of-concept demonstration of functional relevance, showing that the gas lattice formation can persist and reorganize under competitive adsorption, rather than as a claim of best-in-class separation performance.

Pg 26

"…These results provide a proof-of-concept that the ordered adsorbed phase can persist and reorganize under competitive adsorption, generating distinct thermodynamic and kinetic regions within the pore. Once Xenon saturates the shell, Krypton is funneled into a low-barrier core diffusion pathway, whereas Xenon remains trapped in the more strongly bound shell. In this sense, the gas lattice creates a coupled thermodynamic–kinetic separation mechanism that extends beyond site-affinity arguments alone."

We believe this revision better reflects the scope of the present work while still highlighting why framework-templated gas lattices are practically interesting.

2. The phenomenon is mainly demonstrated for xenon. Can the authors comment on whether this concept can be generalized to other gas systems?

We thank the reviewer for this helpful suggestion. To examine how the present framework extends to more complex, non-spherical adsorbates, we applied the same overall workflow to ethane and identified MOF hosts[1] in which the confined adsorbed phase develops an ordered motif. This shows that framework-templated gas-lattice formation is not unique to nearly spherical Xenon, but can also arise for a molecular adsorbate with internal structure.

For ethane, the analysis was performed using the center-of-mass (COM) packing motif of a bulk crystalline BCC ethane phase as the structural reference. Candidate MOFs were first ranked using an ethane COM-based neighbor-count (NC) score, and the highest-ranked structures were then evaluated through snapshot regularity and spatial ordering at the COM level. Under this procedure, one top candidate displayed a clear BCC-like local COM motif under confinement.

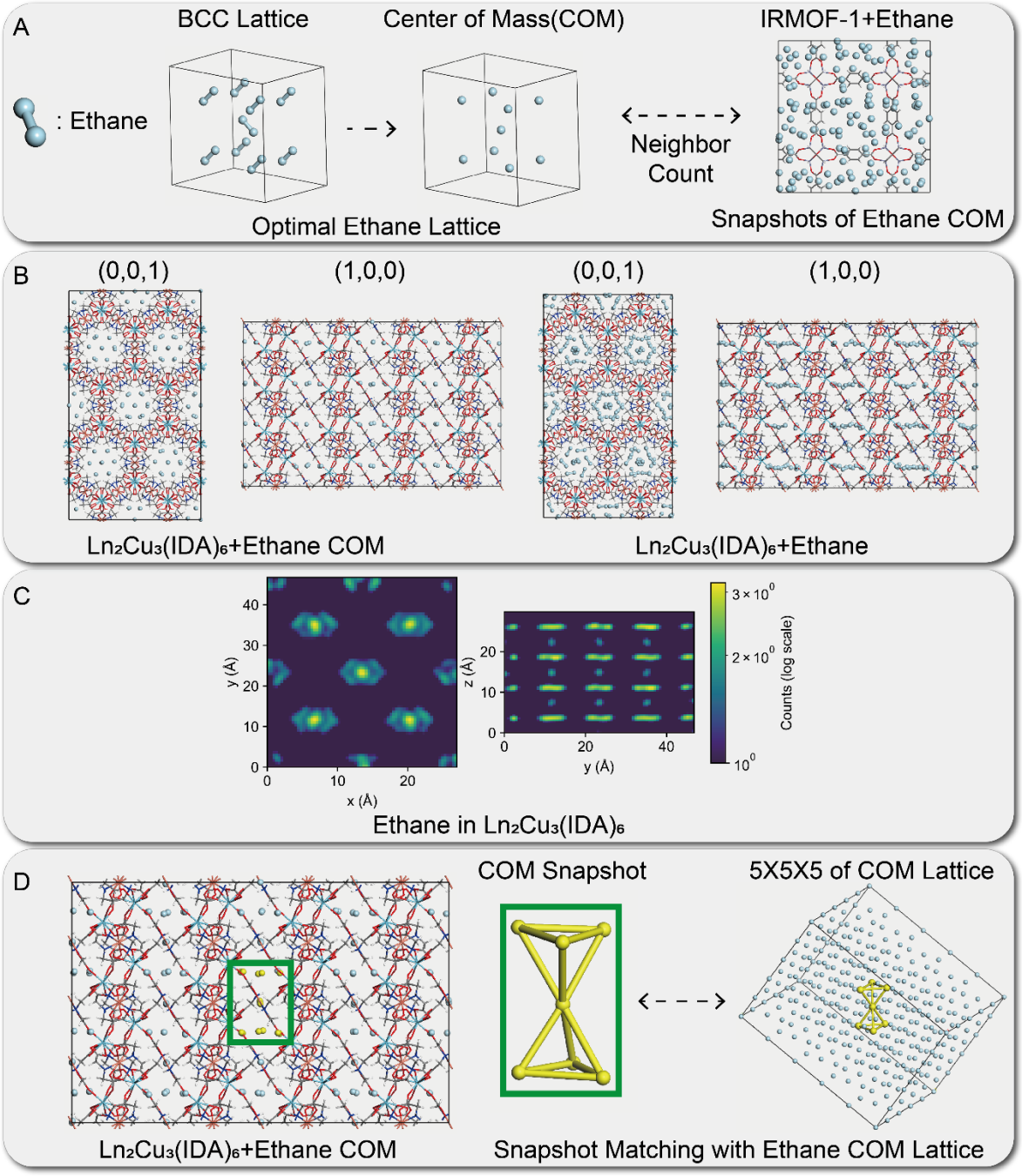
Although the confined ethane motif does not reproduce the bulk crystalline ethane structure exactly, it forms a spatially regular cluster with similar COM distance characteristics and ordering tendency. We therefore interpret the ethane result as direct evidence that the underlying framework-templated ordering principle can extend beyond Xenon to molecular adsorbates. We have revised the manuscript accordingly and clarified that, in such systems, COM-based structural matching provides a natural route for extending the same design logic to more complex guests.

Pg 18

“… Extension to Molecular Adsorbates

Beyond guest size, the same framework-templated gas-lattice concept can also be extended to molecular adsorbates. To test this possibility, we applied the same screening workflow to ethane and searched for MOF hosts that stabilize an ordered adsorbed motif under confinement (Fig. 5). Unlike Xenon, however, ethane is a non-spherical molecular adsorbate and therefore was not evaluated using simple monatomic lattice references such as FCC, BCC, or HCP in the same sense as a one-body gas. Instead, we constructed the ethane metric from the center-of-mass (COM) packing motif of a bulk crystalline BCC ethane phase and ranked candidate MOFs by the similarity of their adsorption snapshots to this ethane-specific ordered reference. This distinction is important because the ordered Xenon lattice is effectively characterized by a relatively regular square-like registry in the projected pore plane, which makes both the design target and the local structural assignment amenable to standardized descriptors such as Neighbor Count. By contrast, the ethane COM arrangement is anisotropic and rectangular rather than square, and the full molecular packing further depends on orientational degrees of freedom. As a result, the same workflow can still identify ordered molecular motifs at the COM level, but the design target is less naturally standardized than in the Xenon case and cannot be captured as completely by the same symmetry-based metrics alone.”

Fig.5



"…Fig. 5: Extension of the gas-lattice workflow to molecular ethane. A) Schematic of the ethane-screening workflow. A BCC ethane lattice reference structure is first converted into a center-of-mass (COM) lattice, which is then used to evaluate GCMC adsorption snapshots through the neighbor-count-based comparison used for monatomic gases. B) Representative views of the selected top candidate, $Ln_2Cu_3(IDA)_6$, shown with ethane COM positions and full ethane molecular configurations along the indicated crystallographic directions. C) Ensemble-averaged ethane density maps in $Ln_2Cu_3(IDA)_6$. D) Local structural correspondence between the confined ethane

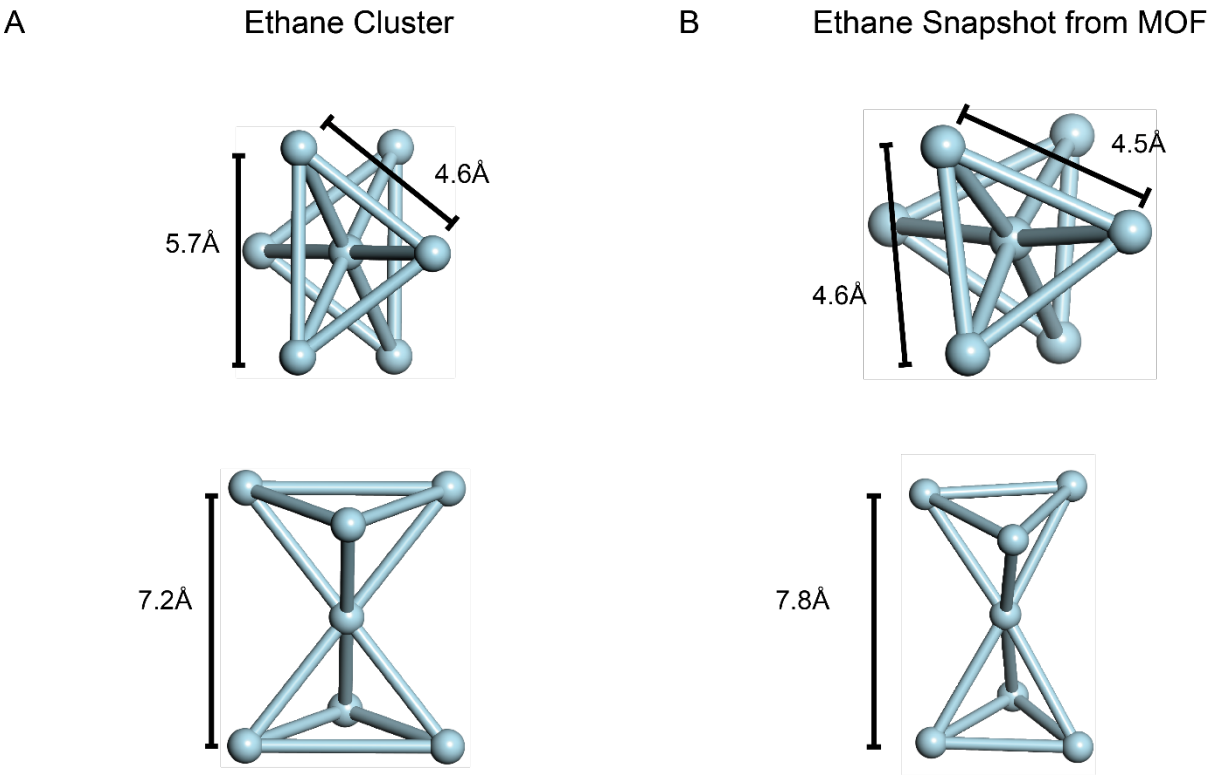
arrangement and the reference COM lattice. A representative cluster from $Ln_2Cu_3(IDA)_6$ (yellow) contains a local ethane COM cluster that matches the reference ordered COM motif embedded in a larger 5 × 5 × 5 COM lattice."

Pg 21

"…Using this procedure, we first ranked candidate MOFs by the ethane COM-based NC score, then selected the most strongly ordered candidates based on their snapshot regularity. By this procedure, we identified MOF hosts, $Ln_2Cu_3(IDA)_6$[32], in which confined ethane develops a clear ordered arrangement. $Ln_2Cu_3(IDA)_6$ does not reproduce the bulk crystalline ethane structure exactly, but it formed a spatially regular cluster with similar COM distance characteristics and ordering tendency, indicating that the framework can still template an ordered molecular packing even when the confined arrangement deviates from the exact bulk crystal structure. Detailed comparison between the bulk ethane crystal and ethane snapshots can be found in the Supplementary Fig. 9. We therefore interpret the ethane result not as exact replication of a bulk molecular solid, but as evidence that the underlying framework-templated ordering principle can extend beyond monatomic guests to adsorbates with internal structure and anisotropic interactions.

The ethane results further demonstrate that framework-templated gas lattice can extend beyond one-body gases to molecular adsorbates. Whereas Xenon is naturally described by translational packing and local coordination, ethane introduces additional structural richness through its anisotropic COM arrangement and molecular character. Nevertheless, the same snapshot-based workflow successfully identified an ordered ethane motif under confinement through COM-based structural matching. More broadly, because our screening framework quantifies ordering directly from adsorption configurations, it can be generalized to other gases by adopting an appropriate ordered reference and applying the same analysis across MOF space."

Supplementary Figure 9



"…Supplementary Fig. 9: Distance and cluster comparison between the reference ethane lattice and the confined ethane motif in the MOF. Comparison of the A) local COM geometry of the reference BCC ethane lattice and B) the ordered ethane cluster extracted from the MOF snapshot."

Pg 35

"…While demonstrated here with noble gases and ethane,"

3. The neighbor-count descriptor is used as a key metric throughout the study. Is it sufficient to reliably characterize gas-lattice formation and material performance?

We thank the reviewer for this important comment. We agree that the neighbor-count (NC) descriptor alone is not sufficient to fully characterize gas-lattice formation or to predict material performance. To avoid overinterpreting NC, we emphasize that candidate validation in this work relies on multiple complementary analyses, including local PTM-based structural identification, ensemble-averaged density maps, and persistence of ordered adsorption features across loading conditions. In other words, NC serves as a computationally efficient first-pass metric, whereas the

presence and robustness of gas-lattice formation must be confirmed by more direct structural observables. We have revised the manuscript to make this distinction more explicit.

Pg 10

"…Accordingly, NC is used here as an initial screening metric, whereas definitive confirmation of gas-lattice formation requires additional structural validation."

The usefulness of NC as an initial descriptor is further supported by our additional extension to ethane, where the same workflow also identifies MOF hosts exhibiting gas-lattice-like ordering. While NC should not be interpreted as a universal or standalone order parameter, these results suggest that it can provide a practical and transferable first-stage metric for identifying candidate systems across chemically distinct adsorbates.

Pg 21

" …Using this procedure, we first ranked candidate MOFs by the ethane COM-based NC score, then selected the most strongly ordered candidates based on their snapshot regularity. By this procedure, we identified MOF hosts, $Ln_2Cu_3(IDA)_6$32, in which confined ethane develops a clear ordered arrangement."

4. The simulations rely on the UFF force field. Could the authors comment on its suitability and limitations for describing gas behavior in these systems?

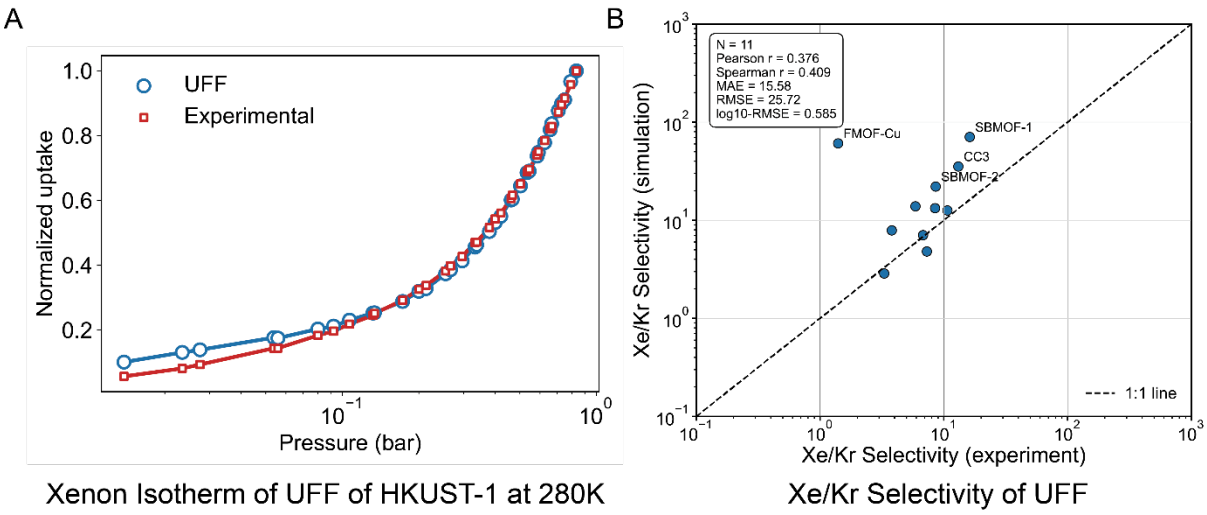
We thank the reviewer for this important comment. We agree that the choice of force field is an important consideration in assessing the robustness of the predicted gas-lattice behavior. In this work, we employed UFF because it is a widely used and computationally practical framework force field for large-scale MOF screening. At the same time, we agree that the original manuscript would have benefited from additional validation of this choice. In the revised manuscript, we therefore clarify both the literature basis for adopting UFF in high-throughput MOF screening[2] and the empirical sanity checks supporting its use in the present system. Specifically, we added comparisons to available experimental adsorption data, including Xenon isotherm of representative MOFs and Xenon/Krypton selectivity trends for different MOFs, and found that the UFF-based simulations reproduce the overall adsorption behavior and the relative Xenon/Krypton selectivity

with reasonable fidelity. We have revised the manuscript accordingly and added the corresponding comparison plots.

Pg 7

"…In these simulations, we employed UFF as a practical framework force field for large-scale screening, consistent with its widespread use in prior high-throughput MOF studies. As a sanity check on this choice, we compared the simulated adsorption behavior against available experimental benchmarks, including representative Xenon isotherms and Xenon/Krypton selectivity trends from previous studies, and found reasonable agreement at the trend level (Supplementary Fig. 2)."

Supplementary Figure 2



Xenon Isotherm of UFF of HKUST-1 at 280K

Xe/Kr Selectivity of UFF

"…Supplementary Fig. 2: Sanity-check comparison of UFF-based adsorption trends against external experimental data. A) Normalized Xenon adsorption isotherm calculated using UFF compared with an experimentally reported Xenon isotherm taken from the literature. Both datasets are normalized to facilitate comparison of the overall pressure-dependent uptake trend. B) Comparison between simulated and experimentally reported Xe/Kr selectivities for a representative set of MOFs. The simulated values were obtained using UFF, while the experimental data were collected from prior literature reports. The dashed line indicates the 1:1 relation. These comparisons support the use of UFF as a screening-level force field that reproduces the overall adsorption and selectivity trends with reasonable fidelity."

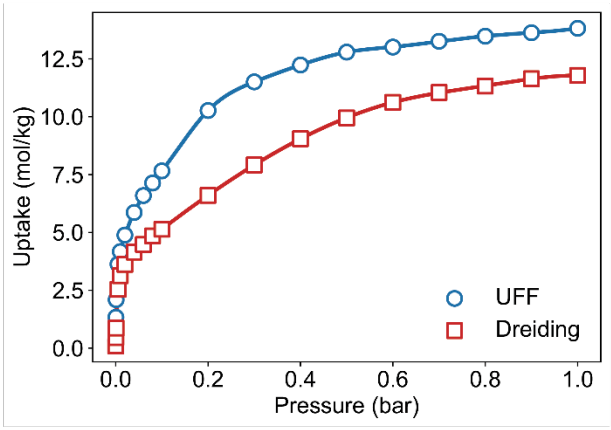
We also acknowledge that UFF is an empirical and non-specialized force field and therefore may not capture all quantitative details of host–guest interactions associated with gas-lattice formation. To further assess robustness, we additionally tested an alternative framework force field, Dreiding, and found that the same qualitative adsorption and ordering behavior is preserved. In particular, although the absolute uptake differs quantitatively, both force fields reproduce the same sequence of shell occupation, pore filling, and the emergence of an ordered gas-lattice-like phase. This consistency indicates that the observed Xenon gas lattice is not an artifact of the UFF description. We therefore present UFF as a practical screening-level model whose utility is supported by qualitative trend consistency, rather than as a uniquely definitive description of the system.

Pg 11

"…To further verify that the observed Xenon gas lattice is not an artifact of the UFF description, we repeated the analysis with different forcefields, Dreiding, and confirmed that the same qualitative gas lattice formation is preserved (Supplementary Fig. 4)."

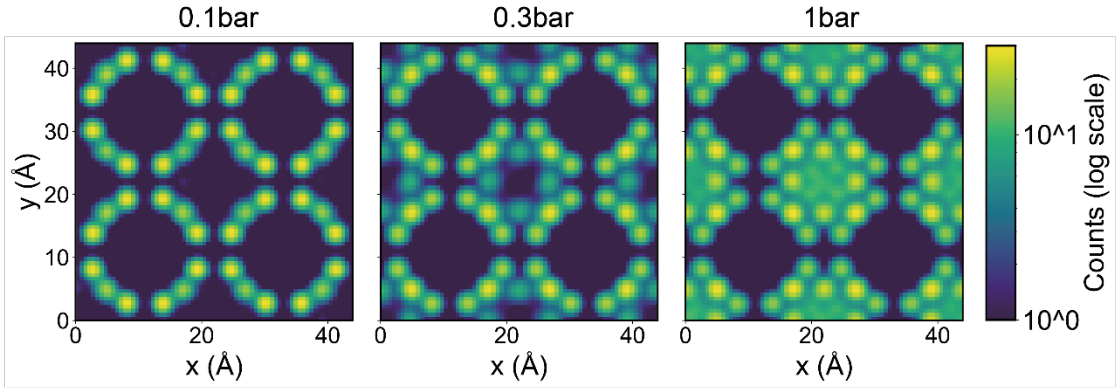
Supplementary Figure 4

A

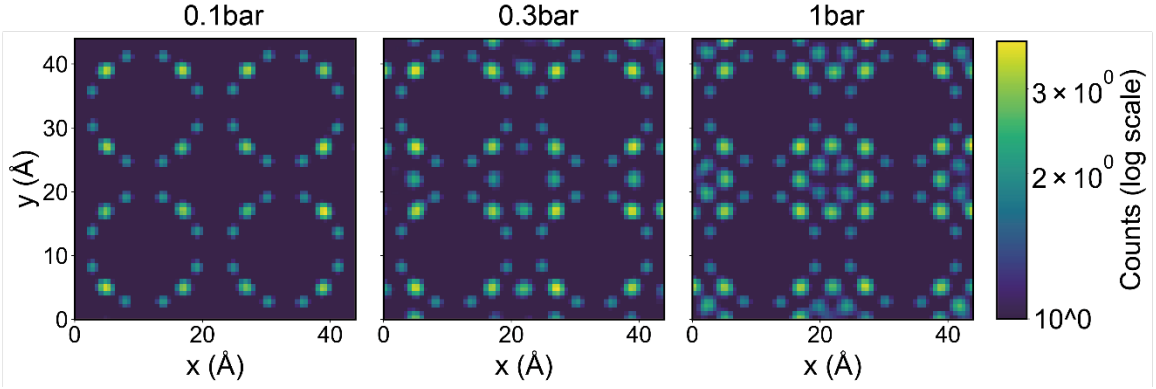


Xenon Isotherm of Co-CAU-36 of UFF and Dreiding

B



C



"…Supplementary Fig. 4: Robustness of Xenon gas-lattice formation with respect to framework force-field choice. A) Xenon adsorption isotherms in Co-CAU-36 calculated using UFF and Dreiding. Although the absolute uptake differs quantitatively between the two force fields, both predict substantial Xenon adsorption over the same pressure range. Ensemble-averaged Xenon density maps in Co-CAU-36 at increasing pressures, calculated using B) Dreiding and C) UFF, respectively. In both cases, the same qualitative evolution is observed: initial shell-site occupation, followed by pore filling, and the emergence of an ordered gas-lattice-like arrangement at higher

loading. These results indicate that the framework-templated Xenon gas lattice is not an artifact of the UFF description, although quantitative details remain force-field dependent."

5. Are the inverse-designed structures potentially experimentally synthesizable?

We thank the reviewer for this important question. We agree that experimental synthesizability is an important consideration for inverse-designed MOFs. In this work, the generated candidates were not constructed from arbitrary hypothetical building units, but from combinations of reported building blocks and known 2D MOF motifs, which increases their likelihood of experimental accessibility. In addition, we screened the designed structures using an external structure validity checker, MOFChecker[3], and only candidates passing these validity checks were suggested as the final candidate. We have clarified this point in the revised manuscript and now discuss the inverse-designed structures more explicitly as synthetically informed candidates, while noting that full experimental realization remains to be demonstrated.

Pg 28

"…Because these candidates were assembled from reported building blocks and known 2D MOF motifs, rather than unconstrained hypothetical components, the resulting design space remains at least partially anchored to experimentally accessible chemistry. In addition, we evaluated the generated structures using MOFChecker and retained only candidates that passed these validity checks for further analysis."

6. Could the authors more clearly compare the proposed adsorbate-phase design concept with conventional performance-guided MOF design strategies?

We thank the reviewer for this helpful suggestion. We agree that this distinction was not sufficiently explicit in the original manuscript. In the revised manuscript, we have clarified that conventional MOF design strategies typically optimize framework properties or bulk performance metrics, such as uptake, selectivity, or heat of adsorption, whereas our approach instead treats the adsorbed phase itself as the design target. In this sense, the goal is not only to identify materials with favorable average performance, but to engineer host structures that template a specific,

spatially organized adsorption state. We have added a corresponding discussion to more clearly position the present work relative to conventional performance-guided MOF design.

Pg 31

"…Beyond identifying inverse-designed pMOFs that promote Xenon lattice formation, these results highlight a useful distinction between the present approach and conventional performance-guided MOF design in the choice of design target. In most MOF discovery workflows, the framework is optimized to maximize bulk metrics such as adsorption capacity, selectivity, or heat of adsorption. By contrast, our approach treats the adsorbed phase itself as an explicit structural target. Rather than asking which framework gives the highest average performance, we ask which framework geometry and pore topology can template a desired guest arrangement under confinement. In this sense, the framework is designed not only as a passive host, but as a scaffold that stabilizes a specific correlated adsorption state. We view this as complementary to conventional MOF screening: performance-based metrics remain essential for evaluating application relevance, while adsorbate-phase design offers an additional route to uncover adsorption mechanisms, cooperative filling behavior, and spatially organized mixed-gas states that may not be apparent from scalar performance descriptors alone."

Reviewer #2 (Remarks to the Author):

The authors introduce the concept of framework-templated gas lattices to describe structurally defined adsorption states in metal-organic frameworks (MOFs), identifying Co-CAU-36 as a host for a pore-spanning Xenon lattice through high-throughput screening. A key motivation of this work is to move beyond traditional adsorbent-focused design by targeting the adsorbed phase itself to better understand uptake and transport.

While the proposed "lattice gas" concept offers an interesting perspective for modeling adsorption behaviors in nanoporous materials, the observed phenomenon is highly constrained to very specific temperatures, a single gas species, and strict framework conditions.

We sincerely thank the reviewer for the careful evaluation of our manuscript and for recognizing the conceptual motivation of this work. We also appreciate the concern that the observed phenomenon may be restricted to specific gases, temperatures, and framework

environments. In the revised manuscript, we have clarified the scope of our claims accordingly and now frame the present study more explicitly as a proof-of-concept demonstration. Detailed responses to the reviewer's specific comments are provided below

Based on the manuscript, the applicability of this concept to other varying systems or broader operating conditions appears extremely limited.

We thank the reviewer for this important comment. We agree that the original manuscript did not sufficiently clarify applicability to other varying systems. In the revised manuscript, we therefore extended the same workflow to ethane and identified MOF hosts[1] in which a framework-templated gas lattice also emerges under confinement, showing that the concept is not limited to monatomic Xenon.

For ethane, the screening used the COM packing motif of a bulk crystalline BCC ethane phase together with an ethane-specific COM-based neighbor-count metric, and the highest-ranked candidates were evaluated using snapshot regularity at the COM level. The resulting top candidate did not exactly reproduce the bulk ethane crystal, but it did form a spatially regular cluster with similar COM distance characteristics. We therefore interpret this as evidence that the underlying ordering principle extends beyond Xenon, while clarifying in the revised manuscript that this generality is at the level of the design concept rather than a universal structural outcome.

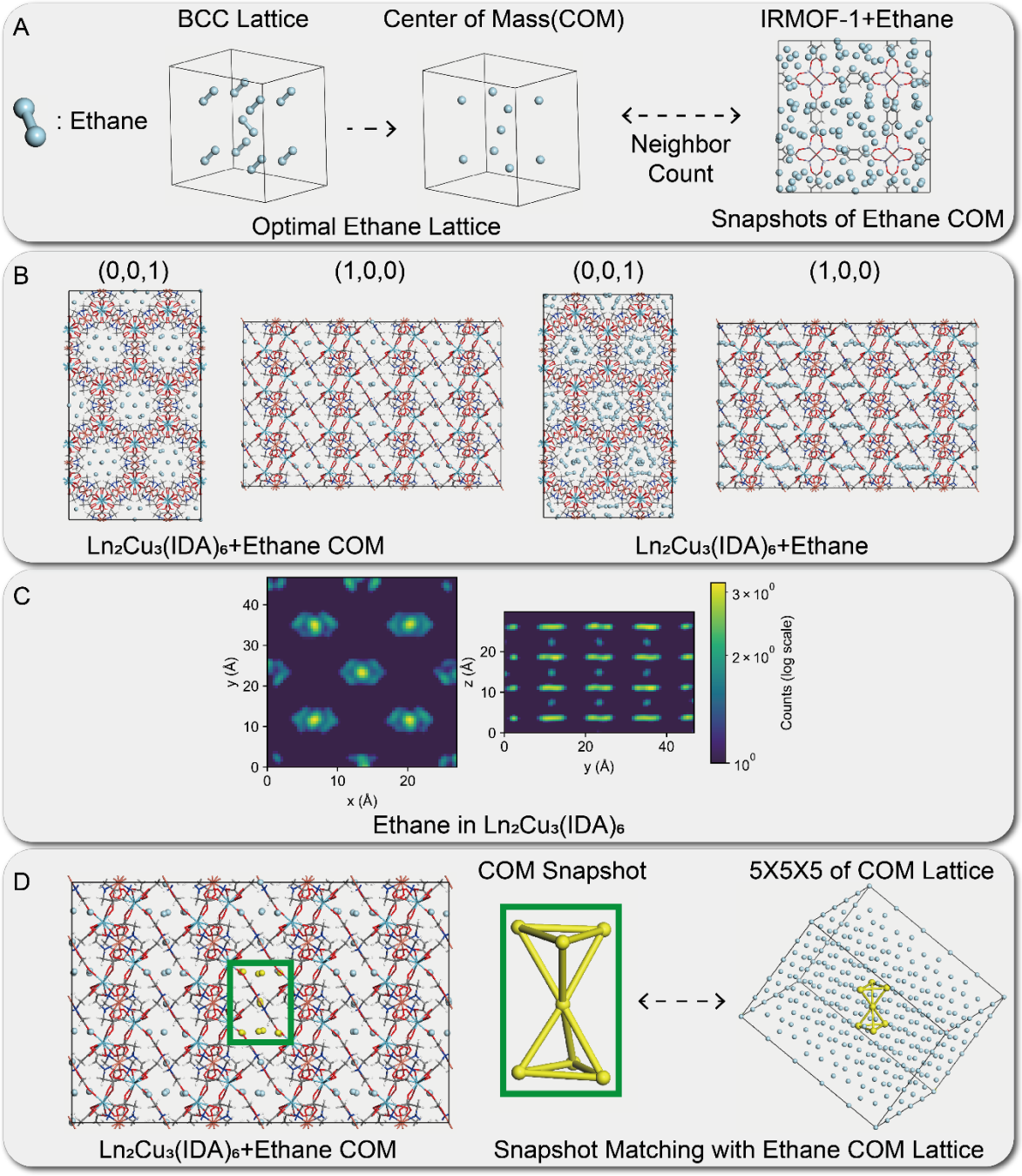
Pg 18

"… Extension to Molecular Adsorbates

Beyond guest size, the same framework-templated gas-lattice concept can also be extended to molecular adsorbates. To test this possibility, we applied the same screening workflow to ethane and searched for MOF hosts that stabilize an ordered adsorbed motif under confinement (Fig. 5). Unlike Xenon, however, ethane is a non-spherical molecular adsorbate and therefore was not evaluated using simple monatomic lattice references such as FCC, BCC, or HCP in the same sense as a one-body gas. Instead, we constructed the ethane metric from the center-of-mass (COM) packing motif of a bulk crystalline BCC ethane phase and ranked candidate MOFs by the similarity of their adsorption snapshots to this ethane-specific ordered reference. This distinction is important because the ordered Xenon lattice is effectively characterized by a relatively regular square-like registry in the projected pore plane, which makes both the design target and the local structural

assignment amenable to standardized descriptors such as Neighbor Count. By contrast, the ethane COM arrangement is anisotropic and rectangular rather than square, and the full molecular packing further depends on orientational degrees of freedom. As a result, the same workflow can still identify ordered molecular motifs at the COM level, but the design target is less naturally standardized than in the Xenon case and cannot be captured as completely by the same symmetry-based metrics alone.”

Fig.5



"…Fig. 5: Extension of the gas-lattice workflow to molecular ethane. A) Schematic of the ethane-screening workflow. A BCC ethane lattice reference structure is first converted into a center-of-mass (COM) lattice, which is then used to evaluate GCMC adsorption snapshots through the neighbor-count-based comparison used for monatomic gases. B) Representative views of the selected top candidate, $Ln_2Cu_3(IDA)_6$, shown with ethane COM positions and full ethane molecular configurations along the indicated crystallographic directions. C) Ensemble-averaged ethane density maps in $Ln_2Cu_3(IDA)_6$. D) Local structural correspondence between the confined ethane

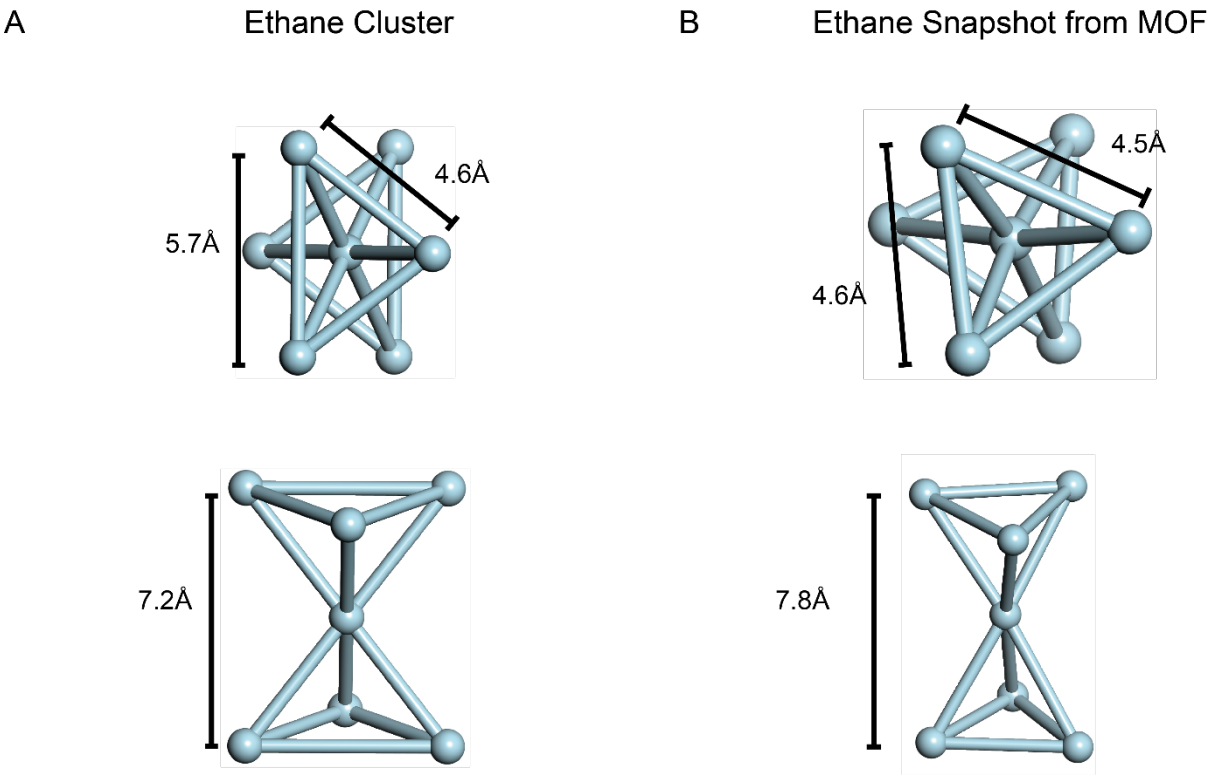
arrangement and the reference COM lattice. A representative cluster from $Ln_2Cu_3(IDA)_6$ (yellow) contains a local ethane COM cluster that matches the reference ordered COM motif embedded in a larger 5 × 5 × 5 COM lattice."

Pg 21

"…Using this procedure, we first ranked candidate MOFs by the ethane COM-based NC score, then selected the most strongly ordered candidates based on their snapshot regularity. By this procedure, we identified MOF hosts, $Ln_2Cu_3(IDA)_6$[32], in which confined ethane develops a clear ordered arrangement. $Ln_2Cu_3(IDA)_6$ does not reproduce the bulk crystalline ethane structure exactly, but it formed a spatially regular cluster with similar COM distance characteristics and ordering tendency, indicating that the framework can still template an ordered molecular packing even when the confined arrangement deviates from the exact bulk crystal structure. Detailed comparison between the bulk ethane crystal and ethane snapshots can be found in the Supplementary Fig. 9. We therefore interpret the ethane result not as exact replication of a bulk molecular solid, but as evidence that the underlying framework-templated ordering principle can extend beyond monatomic guests to adsorbates with internal structure and anisotropic interactions.

The ethane results further demonstrate that framework-templated gas lattice can extend beyond one-body gases to molecular adsorbates. Whereas Xenon is naturally described by translational packing and local coordination, ethane introduces additional structural richness through its anisotropic COM arrangement and molecular character. Nevertheless, the same snapshot-based workflow successfully identified an ordered ethane motif under confinement through COM-based structural matching. More broadly, because our screening framework quantifies ordering directly from adsorption configurations, it can be generalized to other gases by adopting an appropriate ordered reference and applying the same analysis across MOF space."

Supplementary Figure 9



"…Supplementary Fig. 9: Distance and cluster comparison between the reference ethane lattice and the confined ethane motif in the MOF. Comparison of the A) local COM geometry of the reference BCC ethane lattice and B) the ordered ethane cluster extracted from the MOF snapshot."

Pg 33

"…While demonstrated here with noble gases and ethane,"

We also explain more explicitly that the Xenon analysis was not limited to a single operating condition. As shown in the revised discussion and SI, we considered a broader temperature range of 100, 200, and 300 K, and the temperature–pressure window highlighted in the main text was selected as an application-relevant regime in which Xenon remains strongly adsorbed while the onset of lattice formation is still supported by the framework. We agree that this rationale was not sufficiently visible in the original manuscript and have therefore made it more explicit in the revised version.

Pg 12

"…This temperature–pressure window was selected from the broader 100–300 K range examined in this study as an application-relevant regime in which Xenon remains strongly adsorbed and the MOF still supports the onset of lattice formation (Supplementary Fig. 6)."

Furthermore, the calculated lattice constants exhibit a strong dependency on the selected empirical force fields. Although the authors attempt to supplement their study with additional density functional theory (DFT) calculations, this underlying force-field sensitivity raises reasonable doubts regarding the physical realism and robustness of the lattice gas phenomenon in practical environments.

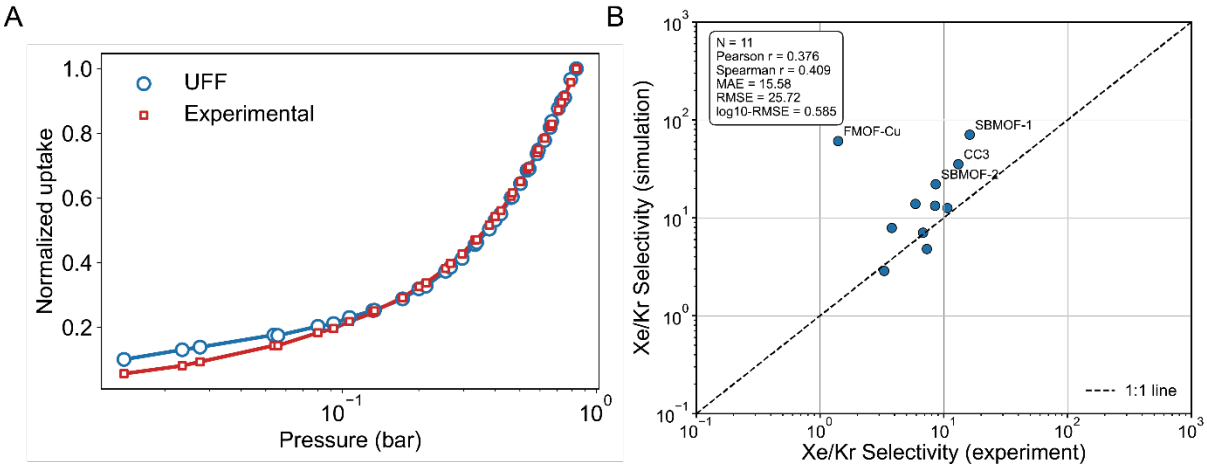
We thank the reviewer for this important comment. We agree that force-field sensitivity is a key issue when assessing the physical realism and robustness of the predicted gas-lattice behavior. In particular, we acknowledge that the precise lattice constants and detailed energetics can depend on the empirical force field used to describe framework–guest interactions. We also agree that this point was not sufficiently addressed in the original manuscript.

In the revised manuscript, we therefore strengthened the validation of our force-field choice. We now clarify the literature basis for adopting UFF as a practical force field for high-throughput MOF screening[2]. Additionally, we added sanity-check comparisons against available experimental adsorption data, including a reported Xenon isotherm and Xenon/Krypton Henry selectivity. These comparisons show that the adsorption trends obtained with UFF are consistent with experimentally observed behavior at the trend level. We have added this validation to the revised manuscript, with the corresponding comparison plots provided in the Supplementary Information.

Pg 7

"…In these simulations, we employed UFF as a practical framework force field for large-scale screening, consistent with its widespread use in prior high-throughput MOF studies. As a sanity check on this choice, we compared the simulated adsorption behavior against available experimental benchmarks, including representative Xenon isotherms and Xenon/Krypton selectivity trends from previous studies, and found reasonable agreement at the trend level (Supplementary Fig. 2)."

Supplementary Figure 2



"…Supplementary Fig. 2: Sanity-check comparison of UFF-based adsorption trends against external experimental data. A) Normalized Xenon adsorption isotherm calculated using UFF compared with an experimentally reported Xenon isotherm taken from the literature. Both datasets are normalized to facilitate comparison of the overall pressure-dependent uptake trend. B) Comparison between simulated and experimentally reported Xe/Kr selectivities for a representative set of MOFs. The simulated values were obtained using UFF, while the experimental data were collected from prior literature reports. The dashed line indicates the 1:1 relation. These comparisons support the use of UFF as a screening-level force field that reproduces the overall adsorption and selectivity trends with reasonable fidelity."

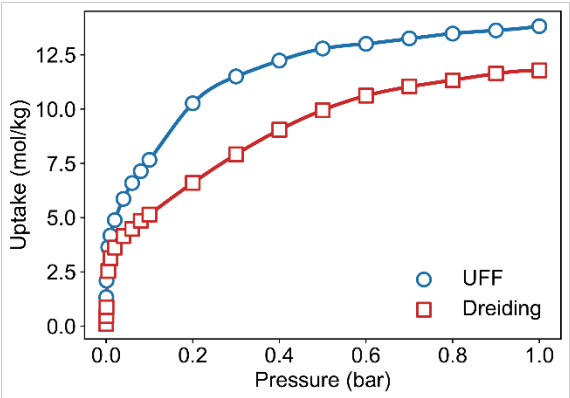
We also directly addressed the reviewer's concern regarding the physical realism and robustness of the predicted lattice-gas behavior. We agree that sensitivity to the empirical force field can reasonably raise doubts if the conclusion depends on a single parametrization. For this reason, we did not rely on UFF alone, but additionally repeated the analysis using an alternative framework force field, Dreiding, and found that the same qualitative gas-lattice behavior is preserved. In particular, although quantitative differences remain, both force fields reproduce the same overall progression from shell occupation to pore filling and ultimately to gas-lattice formation. This consistency supports that the observed Xenon gas lattice is not an artifact of a single force-field choice. We have clarified this point in the revised manuscript.

Pg 11

"…To further verify that the observed Xenon gas lattice is not an artifact of the UFF description, we repeated the analysis with different forcefields, Dreiding, and confirmed that the same qualitative gas lattice formation is preserved (Supplementary Fig. 4)."

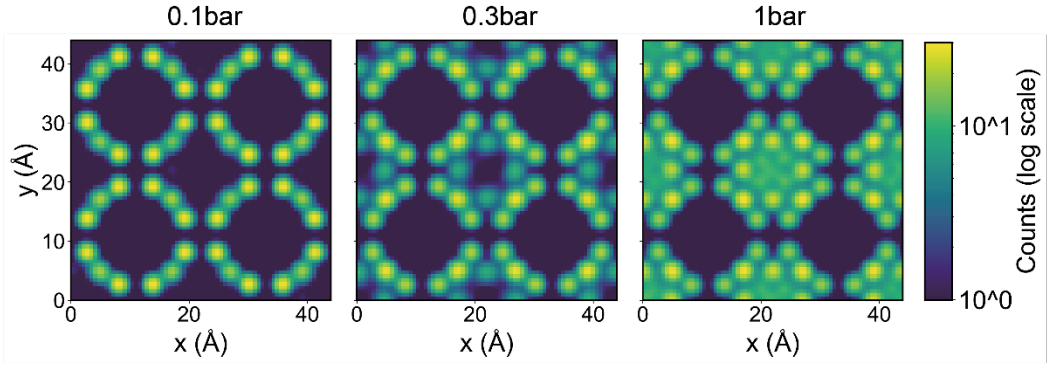
Supplementary Figure 4

A

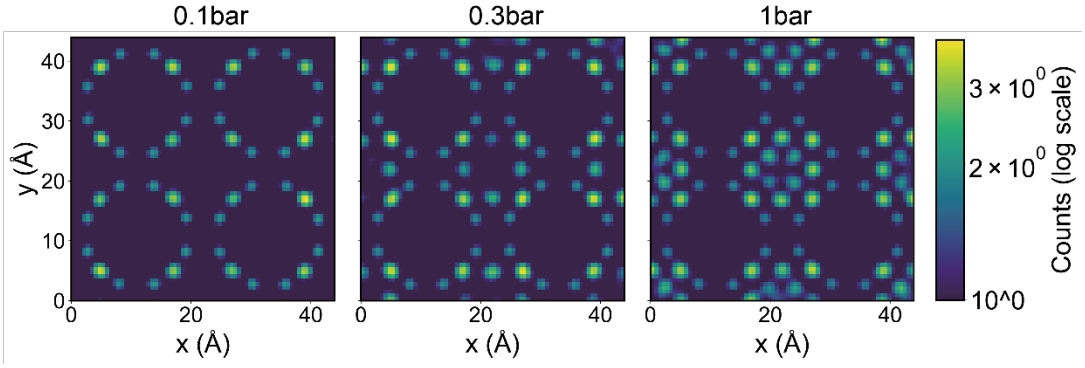


Xenon Isotherm of Co-CAU-36 of UFF and Dreiding

B



C



"…Supplementary Fig. 4: Robustness of Xenon gas-lattice formation with respect to framework force-field choice. A) Xenon adsorption isotherms in Co-CAU-36 calculated using UFF and Dreiding. Although the absolute uptake differs quantitatively between the two force fields, both predict substantial Xenon adsorption over the same pressure range. Ensemble-averaged Xenon density maps in Co-CAU-36 at increasing pressures, calculated using B) Dreiding and C) UFF, respectively. In both cases, the same qualitative evolution is observed: initial shell-site occupation,

followed by pore filling, and the emergence of an ordered gas-lattice-like arrangement at higher loading. These results indicate that the framework-templated Xenon gas lattice is not an artifact of the UFF description, although quantitative details remain force-field dependent."

These results suggest that the predicted lattice-gas phenomenon is not an artifact of a single empirical force field, even though quantitative details such as the exact lattice spacing, degree of mismatch, and precise phase boundaries remain force-field dependent. We therefore interpret the central conclusion as qualitatively robust and physically meaningful at the screening level.

Ultimately, given the highly conditional nature and narrow applicability of these findings, the manuscript does not align with the broad interest and general audience scope required by Nature Communications. While the study offers useful insights into a highly specific system, this after-the-fact approach under restricted conditions makes the work much more appropriate for a specialized journal in physical chemistry or materials science. Therefore, I recommend rejection.

Reviewer #3 (Remarks to the Author):

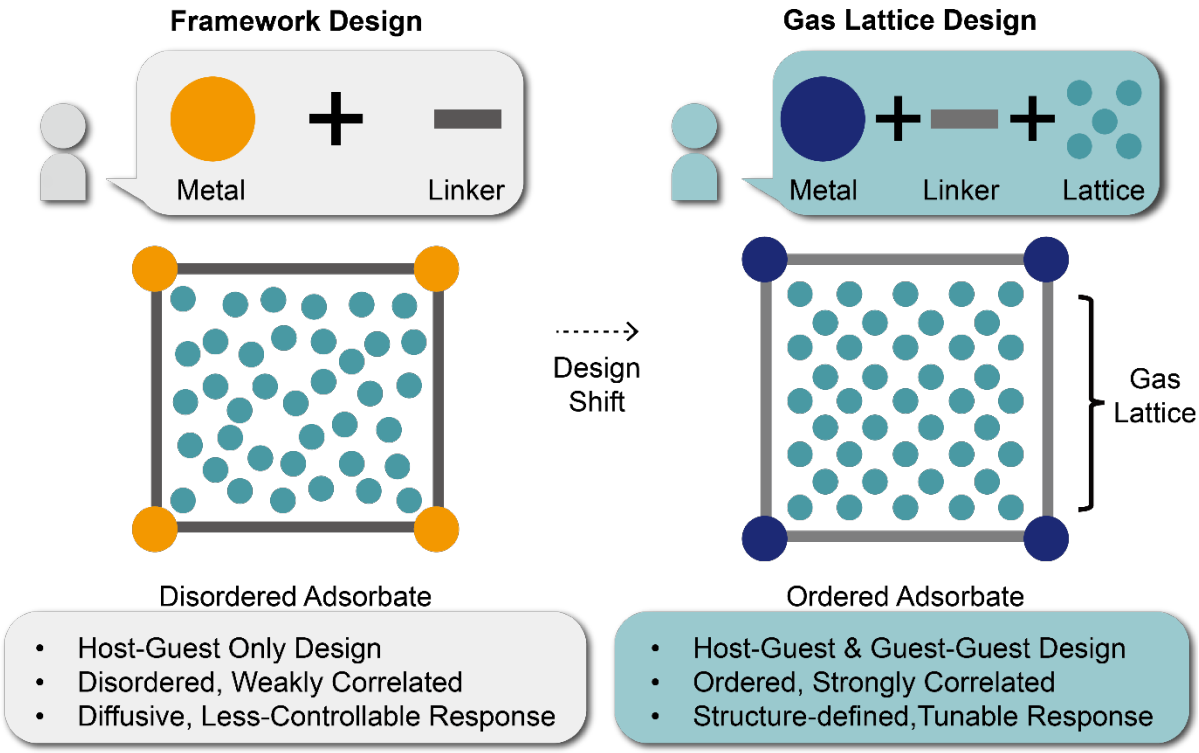
In this work the authors demonstrate that Xe which normally condenses to an FCC fluid can create BCC structures in certain MOFs due to ideal pore size/shape. They also implement a framework for identifying or designing MOFs with the proper structures to achieve this effect. It is an interesting fundamental study combining adsorption and crystallization thermodynamics. I think it needs to be shown a bit more rigorously that this is not a box size effect by doing a convergence test with the simulation box size. I offer some further comments below. I think it should be published with a few edits

We thank the reviewer for the positive evaluation of our manuscript and for the helpful comments. We particularly appreciate the suggestion to more rigorously exclude finite-size artifacts. In the revised manuscript, we have addressed this point through additional box-size convergence analysis and have incorporated the reviewer's further suggestions, as detailed below.

Fig 1: I take some issue with labeling adsorbate interactions as ′weak″ in the left side of figure 1. Polar molecules like water and alcohol can have very strong interactions in a MOF. Similarly I don′t think interactions between the chosen exemplar of Xenon are going to be that strong even when adsorbed to a lattice. Really this is more of an entropic effect than about strength of adsorbate-adsorbate interactions

We thank the reviewer for this helpful comment and agree that the term “weak” was imprecise in this context, as it could be interpreted as referring to the absolute strength of adsorbate–adsorbate interactions rather than the degree of spatial correlation in the adsorbed phase. We intended to distinguish a relatively disordered, weakly correlated adsorption regime from an ordered, correlated adsorbed state, not to imply that all such interactions are intrinsically weak in magnitude. We also agree that, particularly for confined fluids, the emergence of a gas lattice reflects not only energetic stabilization but also an important entropic contribution. In response, we have revised Fig. 1 and the corresponding discussion to replace “weak” with more precise language emphasizing uncorrelated/disordered versus correlated/ordered adsorption behavior.

Figure 1



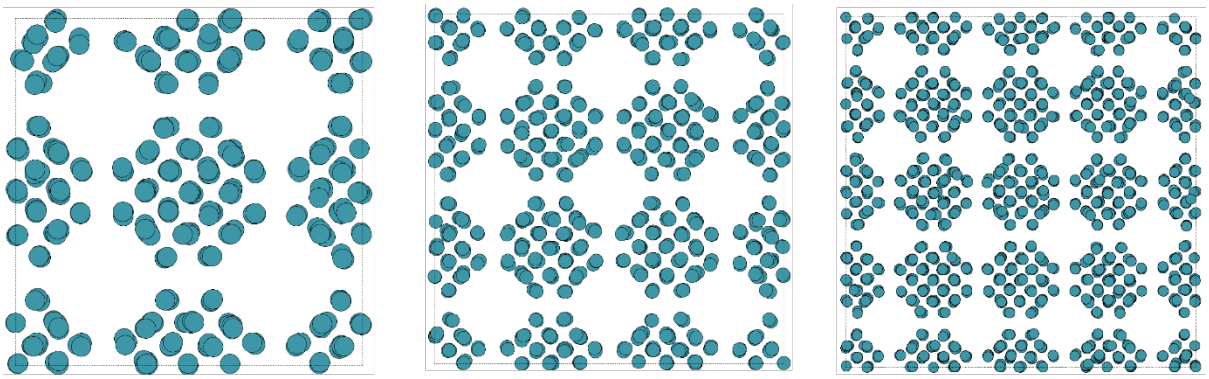
P 11, line 189: it seems the confinement may force the Xe into a BCC lattice which is unusual for a LJ fluid. I think it needs to be checked rigorously this is a real effect and not the result of some finite size artifact. Does the same thing happen if the simulation box is increased?

We thank the reviewer for this important comment. We agree that excluding finite-size artifacts is essential, particularly because BCC ordering is unusual for a Lennard-Jones-like fluid such as Xenon. To address this point, we repeated the simulations using larger supercells and confirmed that the same gas-lattice ordering is retained. The persistence of the ordered adsorbed phase upon increasing the simulation box indicates that the observed BCC-like Xenon lattice is not an artifact of the original cell size. We have added this box-size convergence analysis to the revised manuscript and added the comparison plot in the supplementary information.

Pg 12

"…To exclude the possibility that the observed BCC-like Xenon lattice is a finite-size artifact, we repeated the simulations using larger supercells and found that the same ordered gas-lattice structure is retained (Supplementary Fig. 5)."

Supplementary Figure 5



"…Supplementary Fig. 5: Box-size convergence of the Xenon gas-lattice configuration in Co-CAU-36. Representative Xenon adsorption snapshots obtained from simulations performed with progressively larger supercells. The system size is increased while preserving the same framework topology and adsorption conditions. In all cases, the same qualitative framework-templated ordering is retained, demonstrating that the observed Xenon gas lattice is not a finite-size artifact of the original simulation cell."

Did the authors consider HCP lattices which would generally be more favored over BCC for an LJ fluid?

We thank the reviewer for this important comment. We agree that HCP is a relevant competing packing motif for a Lennard-Jones-like fluid and should be considered alongside FCC and BCC. At the same time, we note that our primary screening descriptor, the neighbor count (NC), is based on RDF-derived local coordination features and is therefore well suited for identifying the emergence of ordered packing, but is less effective for finely discriminating between closely related close-packed motifs such as FCC and HCP, which share very similar local coordination shells and overlapping peak positions (FCC peaks: 4.34, 6.13, 7.525, HCP peaks: 4.32, 6.16, 7.03). For this reason, the present workflow is more robust in distinguishing BCC-like ordering from close-packed alternatives than in making a strict polymorph-level assignment between FCC and HCP at the screening stage. We have revised the manuscript to make this limitation more explicit.

Pg 10

"…We note that HCP is also a relevant competing motif for a Lennard-Jones-like adsorbate. However, because the present screening relies on an RDF-based neighbor-count descriptor, it is more sensitive to the emergence of ordered packing in general than to subtle discrimination between closely related close-packed motifs such as FCC and HCP, which have very similar local coordination shells (FCC peaks: 4.34Å, 6.13Å, 7.53Å, HCP peaks: 4.32Å, 6.16Å, 7.03Å). "

The proposed workflow successfully identifies FCC-like ordered states in the inverse-designed pMOF space, indicating that it captures the formation of close-packed gas-lattice motifs even when fine discrimination between FCC and HCP remains subtle. We therefore view HCP as an important competing reference, while emphasizing that the main objective of the present study is to identify and design a framework-templated gas lattice, rather than to claim complete polymorph-level resolution from NC alone.

I think there needs to generally be more discussion about the effects of entropy in this system which is very important for this kind of ordering. It might help to frame this discussion in terms of the lattice constant of FCC/BCC xenon and compare that to the MOF lattice constant. Is this effect more nuanced than the MOF lattice constant aligning with a multiple of BCC Xe causing BCC to be favored?

We thank the reviewer for this insightful comment. We agree that the original manuscript did not sufficiently discuss the entropic contribution to gas-lattice formation. In the revised manuscript, we now clarify that the observed ordering is not governed solely by energetic site preference, but by a confinement-mediated balance between energetic stabilization and entropic cost. In particular, while the framework provides a periodic binding landscape that favors specific adsorption registries, confinement can also reduce the configurational entropy of the disordered adsorbed phase by restricting its accessible phase space, thereby lowering the entropic penalty associated with ordering. We have further expanded the discussion by explicitly framing the ordering in terms of the commensurability between the characteristic Xenon lattice length scale and the framework-imposed spacing. Importantly, we do not interpret the effect as arising from a simple integer matching between the MOF lattice constant and an ideal BCC Xenon lattice. Rather, the ordering is more nuanced and reflects the combined effects of framework-imprinted energetic

periodicity, geometric frustration, and confinement-modified entropy, which together determine whether a BCC-like adsorbed phase can be stabilized and persist over long length scales.

Pg 31

"…This length-scale matching also suggests that gas-lattice formation should not be viewed as a purely energetic effect or as a simple consequence of the MOF periodicity aligning with an integer multiple of an ideal BCC Xenon lattice. Although ordering reduces configurational freedom, the associated entropic penalty is mitigated under strong confinement, where pore geometry and binding-site topology already restrict the accessible disordered configurations of the adsorbed phase. Accordingly, the degree of ordering is governed not only by adsorption energetics, but also by how closely the framework spacing matches the characteristic Xenon lattice length scale, together with the degree of geometric frustration that this mismatch introduces."

Could the authors offer some comment about how more complicated – non spherical – adsorbates would behave?

We appreciate the reviewer's suggestion and agree that extending the framework to non-spherical adsorbates is an important test of its broader scope. To explore this, we performed an additional analysis for ethane and identified MOF hosts[1] in which the confined adsorbed phase develops an ordered motif. This shows that the framework-templated ordering behavior identified for Xenon is not restricted to nearly spherical guests, but can also arise for a molecular adsorbate with internal structure.

For ethane, the analysis was carried out using the center-of-mass (COM) arrangement derived from a bulk crystalline BCC ethane reference. We first used this COM motif to define an ethane-specific NC-based screening step, and then evaluated the most promising candidates based on the regularity of the resulting adsorption snapshots. Using this procedure, we identified a top candidate exhibiting a clear locally ordered COM motif under confinement.

Although this confined arrangement is not an exact reproduction of the bulk crystalline ethane structure, it preserves a similar distance pattern and spatial regularity, indicating that the same confinement-templated ordering principle remains active. We have revised the manuscript to

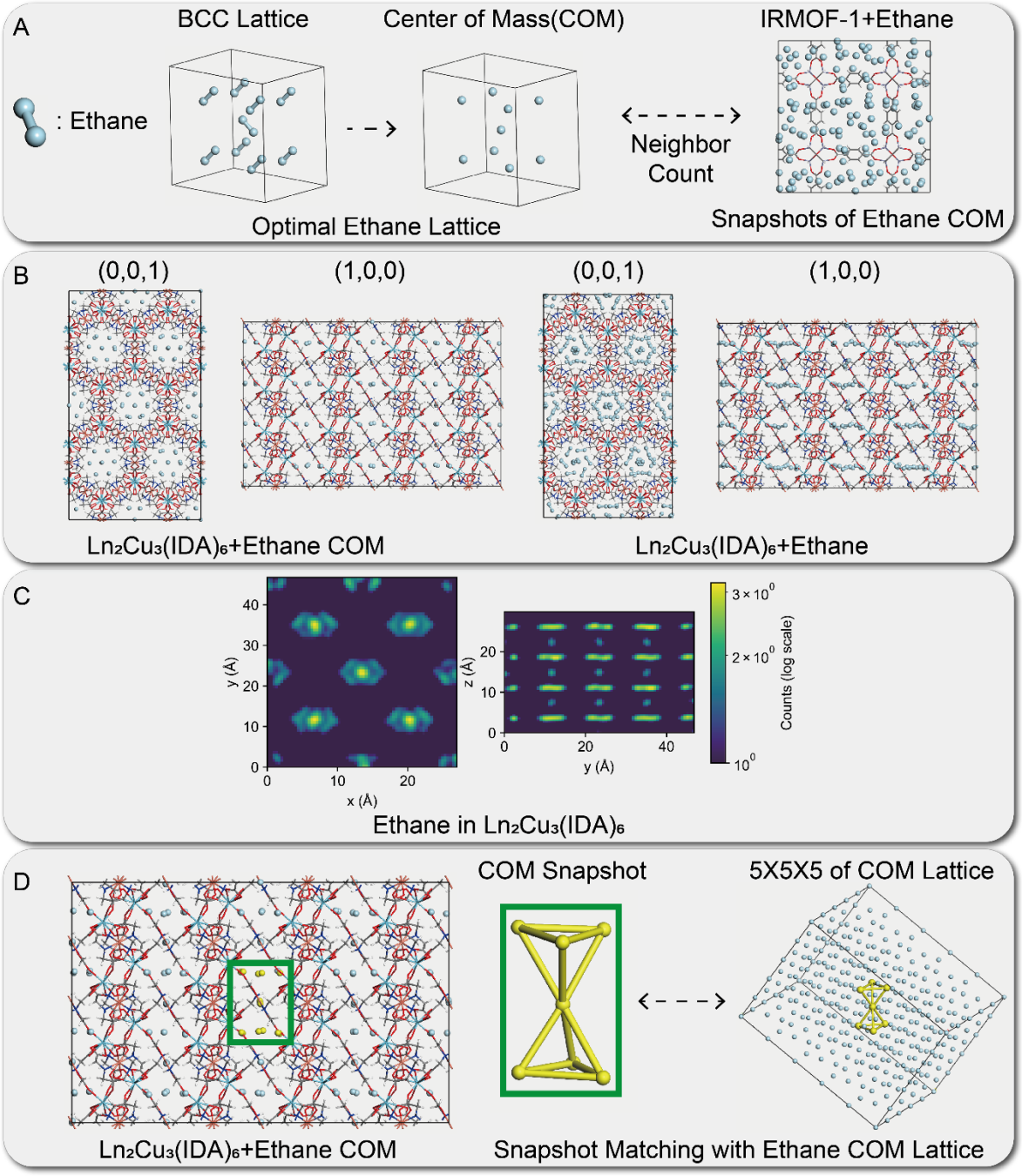
clarify this extension and to note that, for molecular adsorbates, the relevant ordered motif is naturally described at the COM level, providing a practical route to generalize the framework beyond monatomic guests.

Pg 18

"… Extension to Molecular Adsorbates

Beyond guest size, the same framework-templated gas-lattice concept can also be extended to molecular adsorbates. To test this possibility, we applied the same screening workflow to ethane and searched for MOF hosts that stabilize an ordered adsorbed motif under confinement (Fig. 5). Unlike Xenon, however, ethane is a non-spherical molecular adsorbate and therefore was not evaluated using simple monatomic lattice references such as FCC, BCC, or HCP in the same sense as a one-body gas. Instead, we constructed the ethane metric from the center-of-mass (COM) packing motif of a bulk crystalline BCC ethane phase and ranked candidate MOFs by the similarity of their adsorption snapshots to this ethane-specific ordered reference. This distinction is important because the ordered Xenon lattice is effectively characterized by a relatively regular square-like registry in the projected pore plane, which makes both the design target and the local structural assignment amenable to standardized descriptors such as Neighbor Count. By contrast, the ethane COM arrangement is anisotropic and rectangular rather than square, and the full molecular packing further depends on orientational degrees of freedom. As a result, the same workflow can still identify ordered molecular motifs at the COM level, but the design target is less naturally standardized than in the Xenon case and cannot be captured as completely by the same symmetry-based metrics alone."

Fig.5



"…Fig. 5: Extension of the gas-lattice workflow to molecular ethane. A) Schematic of the ethane-screening workflow. A BCC ethane lattice reference structure is first converted into a center-of-mass (COM) lattice, which is then used to evaluate GCMC adsorption snapshots through the neighbor-count-based comparison used for monatomic gases. B) Representative views of the selected top candidate, $Ln_2Cu_3(IDA)_6$, shown with ethane COM positions and full ethane molecular configurations along the indicated crystallographic directions. C) Ensemble-averaged ethane density maps in $Ln_2Cu_3(IDA)_6$. D) Local structural correspondence between the confined ethane

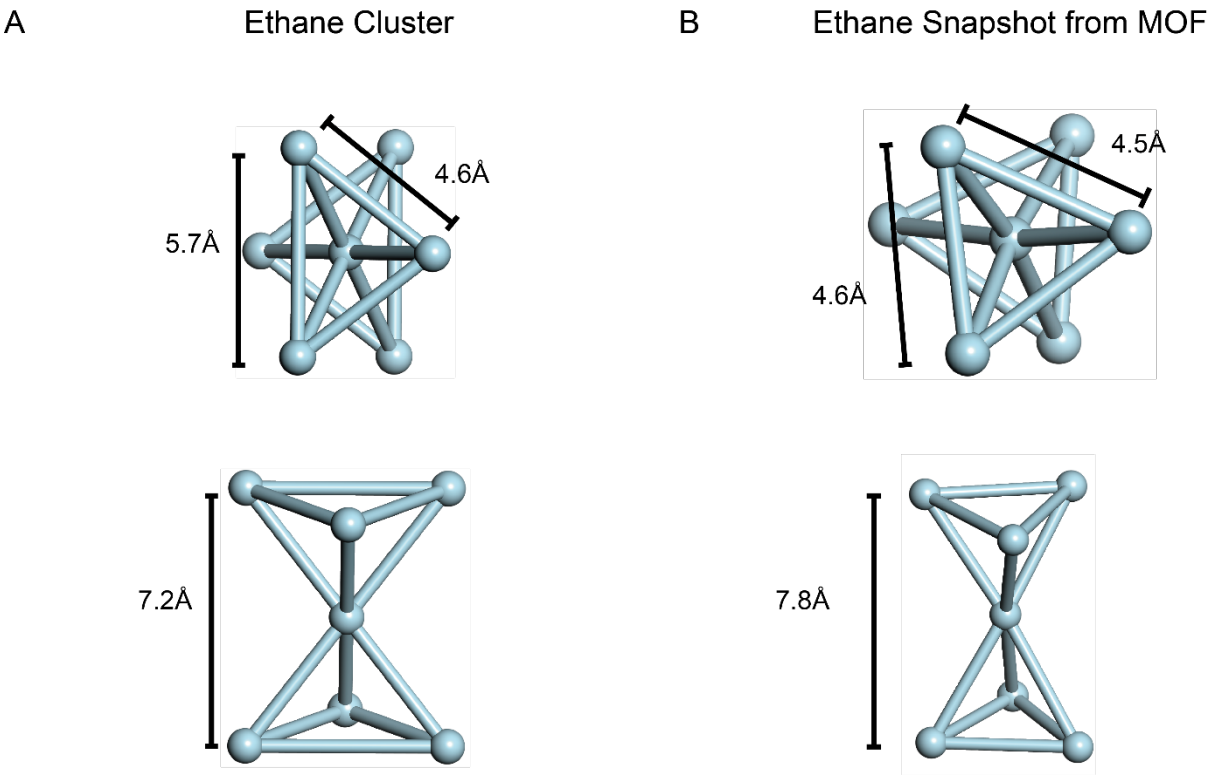
arrangement and the reference COM lattice. A representative cluster from $Ln_2Cu_3(IDA)_6$ (yellow) contains a local ethane COM cluster that matches the reference ordered COM motif embedded in a larger 5 × 5 × 5 COM lattice."

Pg 21

"…Using this procedure, we first ranked candidate MOFs by the ethane COM-based NC score, then selected the most strongly ordered candidates based on their snapshot regularity. By this procedure, we identified MOF hosts, $Ln_2Cu_3(IDA)_6$[32], in which confined ethane develops a clear ordered arrangement. $Ln_2Cu_3(IDA)_6$ does not reproduce the bulk crystalline ethane structure exactly, but it formed a spatially regular cluster with similar COM distance characteristics and ordering tendency, indicating that the framework can still template an ordered molecular packing even when the confined arrangement deviates from the exact bulk crystal structure. Detailed comparison between the bulk ethane crystal and ethane snapshots can be found in the Supplementary Fig. 9. We therefore interpret the ethane result not as exact replication of a bulk molecular solid, but as evidence that the underlying framework-templated ordering principle can extend beyond monatomic guests to adsorbates with internal structure and anisotropic interactions.

The ethane results further demonstrate that framework-templated gas lattice can extend beyond one-body gases to molecular adsorbates. Whereas Xenon is naturally described by translational packing and local coordination, ethane introduces additional structural richness through its anisotropic COM arrangement and molecular character. Nevertheless, the same snapshot-based workflow successfully identified an ordered ethane motif under confinement through COM-based structural matching. More broadly, because our screening framework quantifies ordering directly from adsorption configurations, it can be generalized to other gases by adopting an appropriate ordered reference and applying the same analysis across MOF space."

Supplementary Figure 9



"…Supplementary Fig. 9: Distance and cluster comparison between the reference ethane lattice and the confined ethane motif in the MOF. Comparison of the A) local COM geometry of the reference BCC ethane lattice and B) the ordered ethane cluster extracted from the MOF snapshot."

Pg 35

"…While demonstrated here with noble gases and ethane,"

Reviewer #3 (Remarks on code availability):

I had trouble loading the files from github. Authors should check this is working. It might just be a temporary server issue

We thank the reviewer for pointing this out and apologize for the inconvenience. We carefully checked the GitHub repository and confirmed on our side that the files are currently accessible and can be downloaded without issue. It is possible that the reviewer encountered a temporary server or connectivity problem at the time of access. To improve reliability, we have also

re-checked the repository structure and file links. If access problems persist, we will additionally upload the relevant files through an alternative repository/archive service to ensure stable availability.

References

1 Zhou, B. *et al.* Anomalous dielectric behavior and thermal motion of water molecules confined in channels of porous coordination polymer crystals. *Journal of the American Chemical Society* **133**, 5736-5739 (2011).

2 Banerjee, D. *et al.* Metal–organic framework with optimally selective xenon adsorption and separation. *Nature communications* **7**, ncomms11831 (2016).

3 Jin, X., Jablonka, K. M., Moubarak, E., Li, Y. & Smit, B. MOFChecker: a package for validating and correcting metal–organic framework (MOF) structures. *Digital Discovery* **4**, 1560-1569 (2025).

In this point-by-point response to Reviewers' comments

1. **Black color** – comments from the Reviewers
2. **Blue color** – response to the comments
3. **Green color** – added in the manuscript with page number provided

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Reviewer #1 (Remarks to the Author):

The authors have addressed my concerns, and I have no further major objections to publication. While the conceptual contribution is clear, the manuscript would benefit from a more explicit discussion of how this phenomenon translates to practical performance metrics. A minor suggestion is to further clarify the description of the structural analysis (e.g., NC metric and validation) for better readability. Additionally, a brief discussion on the implications for adsorption or separation performance would further strengthen the practical context.

We sincerely thank the reviewer for the positive assessment of our revised manuscript and for recognizing the conceptual contribution of this work. We also appreciate the helpful suggestions for further improving clarity and practical context.

In response, we have revised the manuscript in two ways. First, we clarified the description of the structural analysis workflow, including the role of the neighbor-count (NC) metric as an initial screening descriptor and the subsequent validation steps used to confirm ordered gas-lattice formation.

Pg 11

…NC is used here as an initial screening metric that quantifies how closely the local adsorption environment resembles the target ordered reference at the level of first-neighbor coordination. In this sense, a high NC indicates that the adsorbed phase is developing a locally lattice-like environment, but it does not by itself establish the persistence, uniformity, or long-range registry of the ordered state throughout the pore. For this reason, NC-based screening is followed by additional structural validation…

Second, we expanded the discussion of practical relevance to more explicitly describe how framework-templated gas lattices may influence adsorption and separation behavior

through cooperative filling, spatially organized adsorption states, and coupled thermodynamic–kinetic effects, while avoiding overstatement of universal performance enhancement.

Pg 35

…From a practical perspective, framework-templated gas lattices influence adsorption behavior by introducing more cooperative and spatially organized filling than in conventional disordered adsorption. Rather than universally maximizing total uptake, such ordering can help concentrate adsorption into a narrower operating window, produce sharper uptake responses, and stabilize distinct filling regimes within the pore. In mixed-gas systems, the same framework-templated ordering can also have implications for separation by promoting species-dependent spatial partitioning and differentiating thermodynamic and kinetic environments. As illustrated here for Xenon/Krypton co-adsorption, one component can occupy the templated shell region while the other is redistributed into a more weakly hindered core region, suggesting a separation mechanism that extends beyond site-affinity differences alone…

We believe these revisions improve the readability and practical framing of the manuscript, and we thank the reviewer again for the constructive suggestions.

Reviewer #2 (Remarks to the Author):

I would like to thank the authors for their detailed responses. Thanks to the in-depth revisions, the manuscript has significantly improved. However, before it can be considered fully suitable for publication, a couple of critical points regarding the validation of the simulation methodology must be addressed more rigorously.

We sincerely thank the reviewer for the careful re-evaluation of our manuscript and for the positive assessment of the revised version. We also appreciate the reviewer’s continued emphasis on rigorous validation of the simulation methodology. We agree that these points are essential for establishing the physical credibility of the proposed gas-lattice phenomenon, and we have addressed them in the revised manuscript as detailed below.

1. The fundamental question regarding whether the observed "crystal formation" is merely a force field (FF) artifact hinges on whether UFF can accurately simulate adsorption behavior and absolute adsorption capacities under cryogenic conditions, specifically at 100 K. Unless the accuracy of UFF in modeling absolute adsorption at 100 K is rigorously validated, it is difficult to accept the findings as a realistic physical phenomenon. Although Supplementary Figure 2 demonstrates that UFF meaningfully captures the trend of adsorption in HKUST-1 at 280 K and shows some correlation with experimental Xe/Kr selectivity, this does not guarantee that UFF will reliably simulate adsorption behavior at 100 K.

Furthermore, regarding the comparison results for HKUST-1, it must be clarified: what were the isotherms normalized against? While demonstrating the validity of UFF through the similarity of normalized isotherms might be acceptable in some contexts, it is inadequate here. Because crystal formation is strictly governed by the absolute amount of adsorption, the simulated adsorption capacity must match experimental values at the specific temperature and pressure of interest. The primary point of comparison should be at 100 K, where crystal formation is most clearly observed. The authors are required to demonstrate that UFF can reproduce experimental adsorption capacities and behavior at such low temperatures. The reliability of the crystal formation—which is the central point of this manuscript—cannot be adequately justified merely by showing a general correlation in adsorption capacity and selectivity under standard conditions.

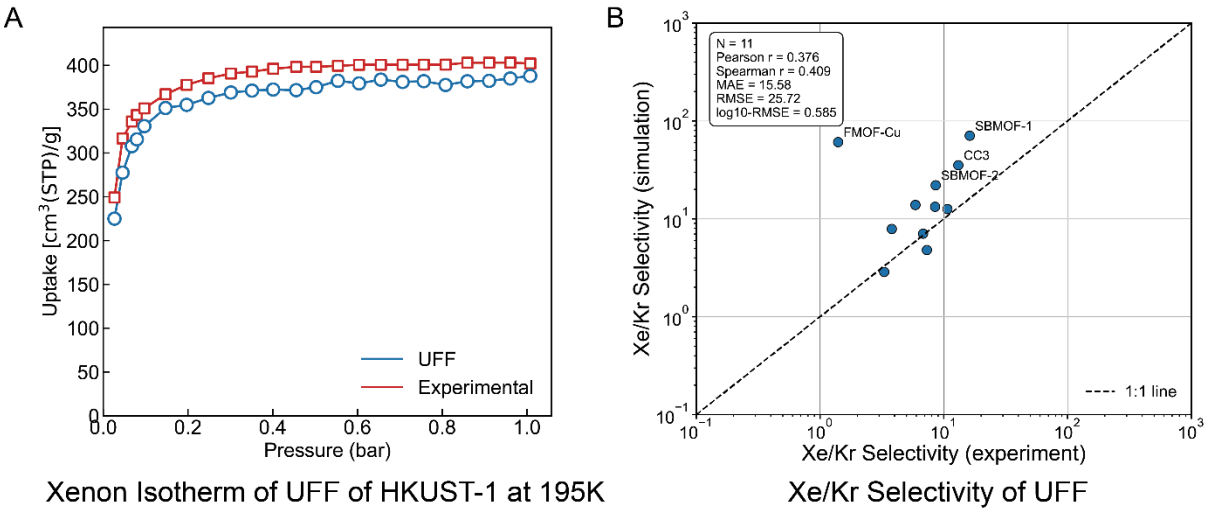
We thank the reviewer for this important and careful comment. We agree that the question of whether the observed gas-lattice formation is a force-field artifact depends critically on whether UFF can reproduce adsorption behavior under the low-temperature conditions relevant to the present study. We also agree that the normalized comparison shown in the previous Supplementary Figure 2 was not sufficient for this purpose, because lattice formation is governed by the absolute adsorption amount rather than by the shape of a normalized isotherm alone.

In the revised manuscript, we therefore replaced this analysis with a more appropriate validation based on absolute adsorption isotherms. Although experimental Xenon adsorption data at 100 K are not available for the benchmark MOF(HKUST-1) we considered, we identified the lowest-temperature experimental dataset available for HKUST-1 at 195 K and directly compared the simulated and experimental adsorption capacities on an absolute basis. This comparison shows that the UFF-based isotherm reproduces the experimental adsorption

behavior with reasonable agreement at the lowest temperature available from experiment, providing a more relevant validation of the force-field description under cryogenic conditions.

We also corrected the presentation of the earlier comparison by explicitly removing the normalized isotherm-based validation as the primary justification. The revised Supplementary Information now clarifies the basis of comparison and presents the validation in terms of absolute uptake, as suggested by the reviewer. We agree that this is the more appropriate test for assessing the physical plausibility of the gas-lattice phenomenon, and we have revised the manuscript accordingly.

Supplementary Fig. 2:



Supplementary Fig. 2: Sanity-check comparison of UFF-based adsorption trends against external experimental data. A) Xenon adsorption isotherm calculated at 195K using UFF compared with an experimentally reported Xenon isotherm taken from the literature…

2. The authors argued that crystal formation is also observed when using the Dreiding force field, presenting this as evidence that it is not a FF artifact. However, as shown in Supplementary Figure 4, the pressure-dependent trends differ significantly between the force fields even at the same temperature. Rather than resolving the issue, this actually highlights the strong dependence of the results on the chosen force field. In other words, even if the phenomenon is computationally possible, the fact that the specific thermodynamic conditions (temperature and pressure) required for crystal formation vary heavily depending on the FF leaves the physical reality of the

phenomenon in question. While I agree with the authors that this work holds value as a "proof of concept," the doubts regarding its actual physical manifestation remain unresolved. To fully address this, the authors need to provide validation through alternative, higher-accuracy simulation methodologies (e.g., ab initio or higher-tier computational methods) or direct experimental evidence.

We thank the reviewer for this important and insightful comment. We agree that the pressure- and temperature-dependent conditions for gas-lattice formation can be sensitive to the choice of force field, and that observing similar behavior with another generic force field alone is not sufficient to quantitatively establish the thermodynamic conditions under which this phenomenon would occur. We also agree that ab initio-level validation provides a more rigorous basis for assessing the physical plausibility of the proposed gas-lattice phase.

In the revised manuscript, we therefore added an additional validation based on density functional theory calculations of representative Xenon adsorption sites identified in the force-field simulations. This analysis examines whether the local adsorption sites underlying the Xenon shell structure are reproduced by a higher-level electronic-structure method, rather than relying solely on comparisons between empirical force fields.

Specifically, we compared the Xenon adsorption shell sites predicted by the force-field calculations with those optimized using DFT in Co-CAU-36. As shown in the revised Supplementary Fig. 8 and Supplementary Table 1, the two representative shell sites are consistently reproduced by DFT. For Site I, the DFT and force-field interaction energies are -7.46 ± 0.14 and -7.21 ± 0.00 kcal/mol, respectively, with a DFT–FF site distance of 0.12 ± 0.03 Å. For Site II, the corresponding values are -4.56 ± 0.05 and -4.34 ± 0.00 kcal/mol, with a site distance of 0.61 ± 0.13 Å.

This agreement indicates that the local adsorption sites underlying the Xenon shell structure are not merely artifacts of the empirical force field, and provides higher-level support for the physical plausibility of the proposed gas-lattice formation mechanism. We have added this DFT-based validation and the corresponding discussion to both the revised manuscript and the Supporting Information.

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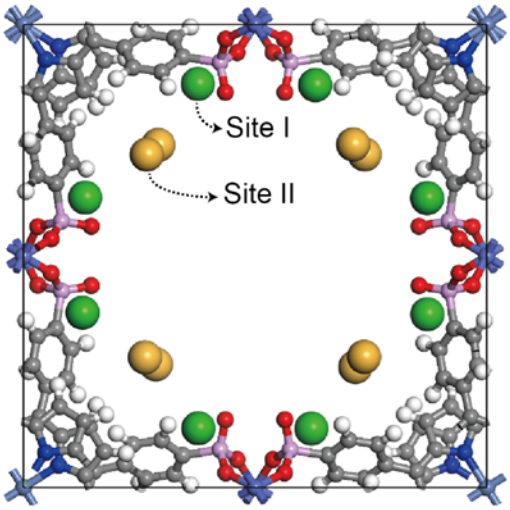
… To further confirm that the Xenon adsorption sites are not force-field-specific, we compared the DFT-optimized Xenon positions with those obtained from force-field calculations. The representative adsorption sites were consistently identified at both levels of theory, and their relative energetic preference was also preserved (Supplementary Fig. 8 and Supplementary Table 1). These agreements support that the force field reliably captures the key Xenon adsorption environments in Co-CAU-36 and that the predicted Xenon lattice arrangement reflects a robust MOF-stabilized configuration rather than a force-field artifact.…

Supplementary Note 1. DFT validation of the Xenon gas lattice and adsorption sites in Co-CAU-36.

… For comparison with the force-field adsorption landscape, UFF-based interaction-energy grids were generated and local minima were identified using a 1.0 Å cutoff criterion. Each DFT-optimized Xenon site was then matched to the nearest UFF grid minimum. The agreement between the DFT and force-field descriptions was quantified by averaging the interaction-energy differences and site-to-site distances between the matched adsorption sites. …

Supplementary Fig. 8:



Supplementary Fig. 8: Consistency of Xenon adsorption shell sites between DFT and force-field calculations in Co-CAU-36. Interaction energies and site-to-site distances confirm the consistency of the Xenon adsorption sites across the two levels of theory.

Supplementary Table. 1:

	$E_{int,DFT}$ (kcal/mol)	$E_{int,FF}$ (kcal/mol)	DFT–FF Site Distance (Å)
Site I	-7.46±0.14	-7.21±0.00	0.12±0.03
Site II	-4.56±0.05	-4.34±0.00	0.61±0.13

Supplementary Table 1. Comparison of Xenon adsorption sites between DFT and force-field calculations. Mean interaction energies and mean DFT–FF site distances are summarized for the representative sites identified in Co-CAU-36.

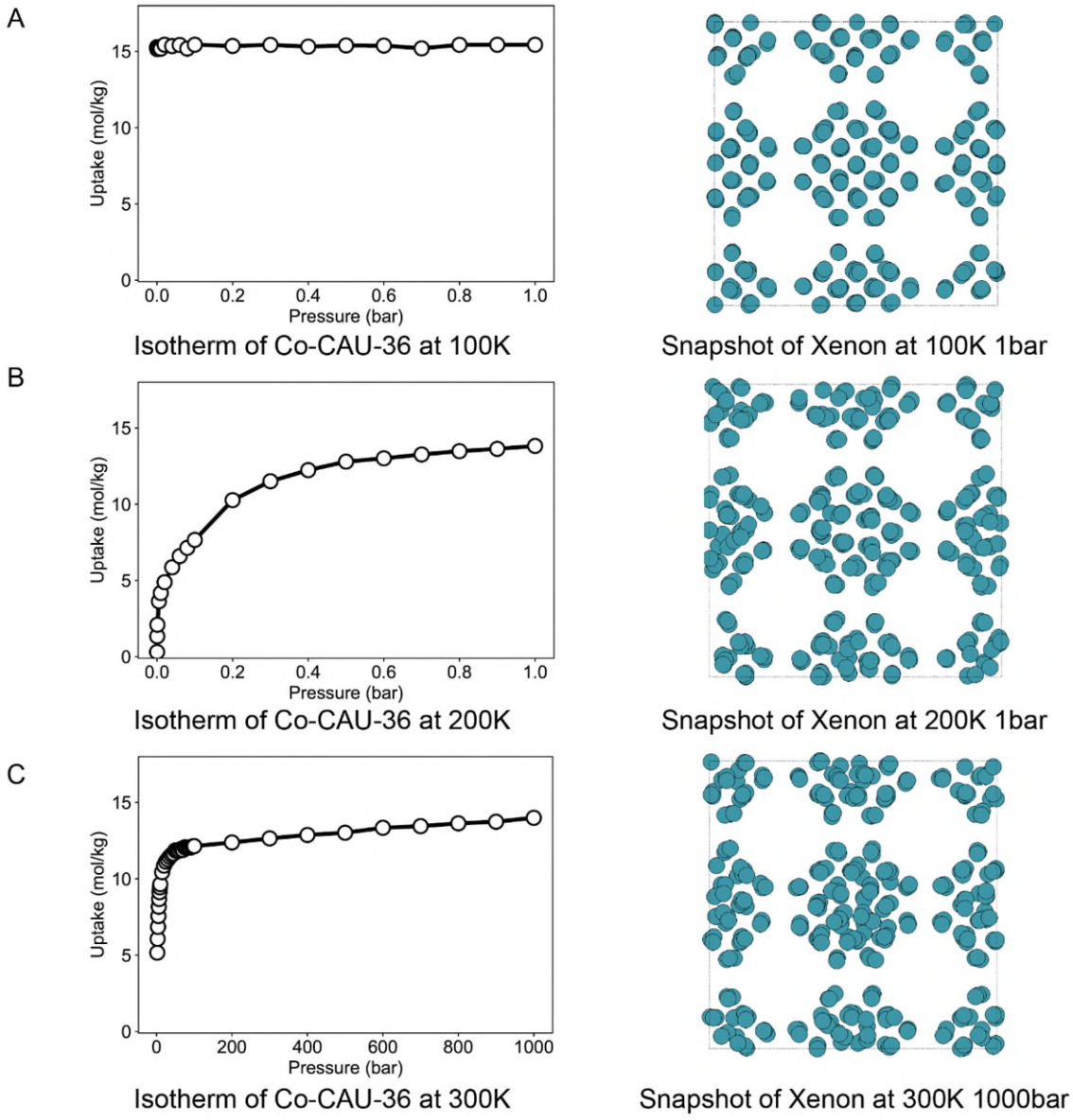
3. Based on the results presented in Supplementary Figure 6, the authors argue that crystal formation is not exclusive to 100 K but can also occur at other temperatures including 300 K. However, to convincingly demonstrate that the filling of molecules near the surface at 300 K truly represents the onset of lattice formation, the authors need to provide evidence at higher pressures. Specifically, it is necessary to show that as the pressure increases further—leading to a higher total adsorption capacity—a well-defined crystal structure actually forms at 300 K, identical to the behavior observed at 100 K.

We thank the reviewer for this important comment. We agree that the previous Supplementary Fig. 6, which showed the 300 K behavior only up to 1 bar, was not sufficient to assess whether Xenon adsorption at 300 K can progress beyond surface adsorption toward substantial pore filling or lattice-like ordering.

In response to the reviewer's suggestion, we extended the 300 K adsorption calculation to much higher pressures, up to 1000 bar, and revised Supplementary Fig. 6 accordingly. The updated isotherm shows that although low-pressure Xenon adsorption is strongly suppressed at 300 K, the uptake increases substantially at high pressure and reaches a pore-filling regime. We note that the extension to 1000 bar was used to reach a Xenon loading comparable to the dense filled states observed at lower temperatures, rather than to imply a practically relevant operating condition. Because adsorption is much weaker at 300 K, substantially higher pressure is required to achieve a similar filling level.

We have revised the Supporting Information to clarify this point. The new comparison shows that substantial pore filling at 300 K requires much higher pressure than at lower temperatures. This additional high-pressure result directly addresses the reviewer's concern by showing that the absence of pore filling in the earlier 300 K snapshot was due to the limited pressure range considered, rather than an intrinsic inability of the system to accommodate a dense Xenon configuration at 300 K.

Supplementary Fig. 6:



Supplementary Fig. 6: Representative adsorption isotherms of Co-CAU-36. Co-CAU-364 isotherm at A) 100K, B) 200K, and C) 300K (left) and corresponding real-space Xenon configurations (right) illustrating distinct adsorption regimes in Co-CAU-36. The 100K snapshot shows near-saturated uptake with a dense, pore-filling arrangement, a pronounced low-pressure uptake with progressive filling toward a high-loading state at 200K, and suppressed low-pressure adsorption with substantial pore filling achieved at very high pressure at 300 K. The 300 K pressure range was extended to 1000 bar to access a Xenon loading comparable to the dense-filled states observed at lower temperatures.