ABSTRACT: Two-dimensional covalent organic frameworks (2D COFs) are a novel class of materials that are ideal for gas storage and separation technologies due to their high porosities and large surface areas. In this work we study the heat transfer mechanisms in 2D COFs with the addition of gas adsorbates, demonstrating the remarkably tunable anisotropic response of the phonon thermal conductivity in 2D COFs during gas adsorption. More specifically, our results from atomistic simulations on COF-5/methane systems show that, as the gas density increases, the cross-plane thermal conductivity along the direction of the laminar pores increases, whereas the in-plane thermal conductivity along the 2D sheets is monotonically decreased. We show that a large portion of heat is conducted along the laminar pore channels by the gas molecules colliding with the solid framework and is directly related to the gas diffusivities.

KEYWORDS: Covalent organic frameworks, anisotropic thermal conductivity, gas infiltration and storage, atomistic simulations

Two-dimensional covalent organic frameworks (2D COFs) constructed from light elements and linked together by strong covalent bonds are an emerging class of porous crystals with a host of unique physical properties that derive from their distinctive structure. For example, their large surface areas and high porosities make them ideal candidates for applications in gas adsorption, separation, and storage. To highlight their potential in these types of applications, COFs have been placed as one of the best candidates for gravimetric H$_2$ storage at 77 K, thus promoting the production of clean fuels for automobiles and reduction of carbon monoxide emission. Moreover, their laminar nanopores and the added flexibility of precisely controlling and organizing different functional building blocks in 2D COFs offer the unique ability to transport ions with enhanced electrochemical accessibility, which has led to their realization as electrodes for supercapacitors and energy storage devices. However, central to advancing 2D COFs for the aforementioned applications, especially where adsorbates can drastically modify their physical properties, is a complete understanding of the fundamental energetic processes that govern their thermal transport efficiency.

In general, an understanding of the energy transport processes in porous crystals has been of great interest to various fields in materials science. However, the intrinsic mechanisms dictating heat transfer at the atomic level for porous crystals with adsorbates has been the subject of debate for the past few decades without a general consensus. This is especially true for heat conduction in filled skutterudites and clathrates, where it was initially suggested that the vibrational “rattler” modes inside the cages and the departure from collective motion with the host lattice were the dominant heat transport mechanisms. However, recent ab initio and neutron scattering experiments have attributed their thermal conductivity to contrastingly different mechanisms such as quasi-harmonic coupling and hybridization of phonon dispersions between the guest and host that are responsible for the lattice thermal conductivity. Similarly, in the case where the guest species are not necessarily constrained inside a cage and are free to flow throughout the crystal such as in a metal–organic framework (MOF), molecular dynamics (MD) simulations have shown that increasing the gas concentration can lead to an overall increase in the thermal conductivity of the MOF. In contrast to these results, recent computational studies with support from thermoreflectance measurements have conclusively shown that gas molecules serve to lower the thermal conductivity of the MOFs due to scattering with the crystalline framework.

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These aforementioned studies lay the groundwork for understanding heat transfer mechanisms in porous crystals. Yet the lack of general consensus along with the inherently different pore geometries in 2D COFs in comparison to their MOF cousins make it difficult to extend the results from these studies to gain insights into the heat transfer mechanisms in 2D COFs. Moreover, studies focusing on heat transfer across COFs have been nonexistent in prior literature, which shrouds the understanding of various mechanisms that could be dictating heat flow in these novel materials. For example, the gas adsorbates could create additional heat transfer pathways inside the pores to facilitate the overall thermal transport or they could scatter with the vibrations of the crystalline solid to create resistance and lower the thermal conductivity. Given the anisotropy in the structure of 2D COFs, these processes could also have varying effects along the direction of the pore alignment with weaker van der Waals interactions (cross-plane) as opposed to that along the direction of the 2D layers with strong covalent bonds (in-plane). Therefore, in this work we seek to understand these mechanisms in detail by conducting systematic atomistic simulations on model 2D COFs with varying gas densities adsorbed in their pores. Our results reveal the inherent anisotropic nature of thermal transport in 2D COFs, which can be manipulated by changing the adsorbed gas density. Specifically, we find that, as the gas density increases, the thermal conductivity along the 1D pore channels (or the cross-plane direction) increases drastically, whereas the thermal conductivity along the 2D layers is monotonically decreased. We also find that a large portion of heat is conducted in the cross-plane direction by the gas molecules colliding with the solid framework. This additional “heat pathway”, however, does not enhance heat transfer in the in-plane direction and rather leads to enhanced vibrational scattering due to solid–gas collisions, thus resulting in a reduced thermal conductivity along the layers with gas infiltration. We show that the increase in thermal conductivity along the direction of the pore channels for infiltrated COFs is directly related to the diffusivities of the gas molecules. These findings could have major implications on technologies based on 2D COFs for gas separation, catalysis, and storage.

We base our calculations on the prototypical COF-5 structure that has a hexagonal lattice with porous sheets separated by a ∼0.34 nm interlayer spacing and stacked neatly in an eclipsed fashion. Since pressure can drastically modify the gas dynamics inside the pores, we prescribe 0 bar pressure on all three periodic boundaries in our simulations. Schematic representations of our equilibrated computational domains for COF-5 and COF-5 infiltrated with gas adsorbates are shown in Figure S1. To calculate the thermal conductivity, we implement the Green–Kubo (GK) approach under the equilibrium molecular dynamics (EMD) framework with a time step of 0.5 fs for all simulations. We verify our GK predictions by comparing the results for the in-plane thermal conductivity of our COF-5 structure with those calculated using the nonequilibrium MD method (see the Supporting Information for further details of the simulations). We employ the widely used adaptive intermolecular reactive empirical bond order (AIREBO) potential to describe the interatomic interactions. Consistent with previous atomistic simulations on infiltrated MOFs, we chose methane as our model gas adsorbate. The interactions between the methane and the solid framework are also described by the same potential. As we are interested in understanding the influence of host–guest interactions on the thermal transport characteristics of 2D COFs in general as opposed to their material-specific properties, our choice of the interatomic potential is sufficient to provide the necessary qualitative insight into the differing thermal transport processes of 2D COFs with and without gas adsorbates. All simulations were performed with the LAMMPS package. Figure 1a shows our GK-predicted thermal conductivity of the COF-5 structures as a function of gas density at room temperature. For the pristine COF-5 structure, the thermal conductivity in the cross-plane direction with weaker van der Waals interactions is lower by a factor of 3 in comparison to the thermal conductivity in the in-plane direction with the stronger covalent bonds. However, as the gas density is increased inside the pores, the cross-plane thermal conductivity increases, whereas that in the in-plane direction decreases monotonically, thus leading to an overall decrease in the anisotropy. The gas adsorbates contribute negligibly to the heat conduction in the in-plane direction, and all of the heat is carried by the covalently bonded solid portion, as shown in Figure 1b. In contrast, the contribution after the addition of the gas adsorbates to the total thermal conductivity in the cross-plane direction is significantly enhanced, as shown in Figure 1c. In fact, the total thermal conductivity can be increased by as much as ∼80% with the adsorption of gases at ∼4.7 molecules/nm³, as shown in Figure 1d. Calculations of the diffusivities of the gas molecules reveal that the diffusivities in the in-plane directions are much lowered in comparison to those in the cross-plane direction (see Figure S8), where the gas molecules are not necessarily constrained and are free to diffuse along the pore channels. Moreover, we find that there is negligible change in the contribution of the
solid framework to the total thermal conductivity in the cross-plane direction, suggesting that phonon scattering due to gas adsorbates does not limit the cross-plane heat conduction in the solid framework.

We attribute the increase in gas molecule contributions to increased collisions with the crystalline pores and not to gas–gas collisions for two reasons. First, the convective contribution is negligible and all the heat is conducted through the virial contributions both in the solid and the gas (see the Supporting Information for details). Additional simulations of computational domains containing only the gas molecules (at the same concentration or at higher densities in comparison to that inside the COF-5 pores) reveal that the thermal conductivity of the bulk gas is drastically lower than the thermal conductivity of the gas inside the COF-5 structure, as shown in Figure S7. Second, we calculate the diffusivities of the gas molecules in our COF-5 pores to be on the order of 10^{-3} cm^{2} s^{-1} (see Figure S10), which is 3 orders of magnitude lower than the typical diffusivities for bulk gas. This implies that the diffusion of gas molecules inside the COF-5 pores is unlike that of the bulk gas and is better described with Knudsen flow or surface diffusion where the diffusivity in comparison to the bulk is drastically lowered by collisions with the crystalline pores.

As shown by the results in Figure 1, gas infiltration has a significantly different effect on the vibrational heat transfer in the in-plane and cross-plane directions. This is also evident from the differences in the vibrational density of states (DOS) in the two directions, as shown in Figure 2. For both directions, there are negligible changes in the DOS with the addition of gas molecules. Even though the DOS in the cross-plane direction encompasses a broad spectral range (0.1–50 THz), our spectral heat flux calculations of the solid framework as shown in Figure 2b suggest that the heat in the cross-plane direction is mainly carried by vibrations lower than 10 THz; the cross-plane spectral heat flux in the solid is not affected by the addition of gas adsorbates. For comparison, the DOS of the gas, which is limited to the low-frequency region (<1 THz) is also shown in Figure 2a. Similarly, the DOS in the in-plane direction as shown in Figure 2c shows a negligible change with the addition of gas molecules inside the COF-5 pores. However, the spectral heat flux in the in-plane direction is lowered for the entire frequency range due to the scattering of the gas molecules with the pore walls (see Figure 2d). The decrease in thermal conductivity in the in-plane direction as the gas density is increased can only be due to increased phonon scattering (over a broad frequency range, as suggested by the spectral heat flux calculations). We note that although our DOS calculations for the solid framework lack the resolution to identify the additional channels of heat transfer through the solid–gas collisions, the DOS calculations of the methane gas inside the pores in comparison to that in the bulk phase shows a drastic increase in the 0–3 THz range (see Figure S11).

We can gain further insights into the anisotropic heat transfer mechanisms in 2D COFs (with and without gas adsorbates) by considering the temperature-dependent thermal conductivities for the pristine and filled COF-5 structures, as shown in Figure 3.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** (a) Vibrational density of states in the cross-plane direction for the COF-5 structure with and without gas adsorbates (at ~4 molecules nm^{-3}). (b) Complementary spectral heat flux calculations in the cross-plane direction for the COF-5 structure with and without gas adsorbates. (c) Vibrational density of states in the in-plane direction for the COF-5 structure with and without gas adsorbates (at ~4 molecules nm^{-3}) showing a broader spectral range (due to the stronger covalent nature of bonding along the 2D sheets) in comparison to that in the cross-plane direction. (d) Complementary spectral heat flux calculations in the in-plane direction for the COF-5 structure with and without gas adsorbates, showing a reduction in the heat flux across the entire spectral range with gas adsorbates.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Thermal conductivity in the (a) in-plane and (b) cross-plane directions for the COF-5 structures with and without gas adsorbates (at a gas density of 3.7 molecules nm^{-3}).

For defect-free crystalline materials in general, the temperature-dependent thermal conductivities usually demonstrate a \( \kappa \propto T^{-1} \) temperature trend, which is mainly attributed to anharmonic phonon–phonon scattering processes above the Debye temperature of the solids (e.g., Umklapp scattering \( 5,38 \)). In comparison to the in-plane direction, anharmonicity is shown to have a larger contribution to the thermal conductivity in the cross-plane direction, as suggested by their respective temperature trends (see Figure 3). However, the addition of gas molecules drastically changes the temperature trends in both the in-plane and cross-plane directions, as shown in Figure 3a,b, respectively. We note that the contribution from the electrons to the total
thermal conductivity in the 2D COF structures studied in this work is negligible due to the relatively large band gaps. Through first-principles calculations, Zhu et al. have shown that (depending on the porosity) the band gap for these layered materials can range from 2.65 to 7.9 eV for similar 2D COFs. Furthermore, electrical conductivity measurements on similar pristine 2D COFs have confirmed their semiconducting nature. As such, for the temperature range considered in this work, we can assume that the heat conduction in 2D COFs is solely due to the lattice contributions.

For the in-plane direction, the reduction in thermal conductivity is much more pronounced as the temperature is lowered. Furthermore, the in-plane thermal conductivity for the filled COF-5 structure does not change throughout the temperature range (even for COFs with gas densities as low as ~0.5 molecules/nm³; see Figure S5), which further solidifies our claim that collisions due to gas and the crystalline pore walls lead to drastic vibrational scattering and thus lowered thermal conductivities in the in-plane direction. In contrast, the thermal conductivity for the filled COF-5 in the cross-plane direction increases with increasing temperature. We find that, as the temperature is increased, the contribution to the total thermal conductivity in the cross-plane direction due to infiltration of gas molecules increases monotonically throughout the temperature range (see Figure S6a). The similar trend in the increase in gas diffusivities with temperature shown in Figure S6b suggests that the linearly increasing cross-plane thermal conductivity is most likely due to higher mobilities of the gas molecules at higher temperatures. As the temperature increases, the diffusivity of the gas increases, which leads to higher kinetic energies of the gas molecules and a concomitant increase in the cross-plane thermal conductivity. As discussed above, we attribute this to enhanced guest–host interactions (leading to an increase in solid/gas thermal boundary conductance) and not solely due to gas–gas collisions.

To investigate how the diffusivities of the infiltrated gas inside the laminar pores in 2D COFs affect the overall thermal transport, we performed additional simulations on modified COF-5 structures by adding phenyl rings on the pore walls, as shown in the close-up views of the computational domains comparing the internal pore geometries in Figure 4a–c for our COF-5, COF-5-2R, and COF-5-4R structures, where “R” stands for “rings”. As is clear, the phenyl rings modify the internal pore geometry by reducing the empty pore volume that the gas molecules can diffuse through. We note that similar incorporations of aromatic and functional groups into the pore walls of 2D COFs have been experimentally fabricated to mainly aid catalytic processes and to reinforce interlayer interactions. The predicted thermal conductivities in the in-plane and cross-plane directions for our COF-5, COF-5-2R, and COF-5-4R are shown in Figure 4d. For computational domains without the gas adsorbates, adding the phenyl rings on the pore walls leads to an increase in the mass densities, which increases the cross-plane thermal conductivities for the pristine COFs. However, the in-plane thermal conductivities decrease with the addition of the phenyl rings on the pore walls, which can be attributed to additional vibrational scattering introduced by the attached phenyl rings along the covalently bonded layers. This is also evidenced by the negligible change in the in-plane thermal conductivities with the addition of gas molecules (at a density of ~4.5 molecules/nm³) in the pore channels for the structures with the phenyl rings. The additional vibrational scattering due to gas molecules does not significantly affect the in-plane thermal conductivity in these structures, which is already lowered due to the scattering introduced by the additional phenyl rings.

The incorporation of the additional phenyl rings on the pore walls lead to reduced space for the gas molecules to freely diffuse through, thus decreasing their mobilities (Figure 4e). As such, the relative increase in cross-plane thermal conductivity due to gas adsorbates in the COF-5-2R and COF-5-4R structures in comparison to that in the COF-5 structure is reduced, as shown in Figure 4f. Therefore, adding the phenyl rings to the pore walls and restricting the pore channel volume that the gas molecules can occupy can drastically lower the diffusivities and concomitantly lead to reductions in the overall heat transfer.

Figure 4. Close-up views highlighting the internal pore geometries of (a) COF-5, (b) COF-5-2R, and (c) COF-5-4R structures. (d) Thermal conductivity for the three different structures with varying densities. (e) Mean square displacements of the gas molecules inside the pore channels of the three different COFs as a function of the simulation time. (f) Comparison of the decrease in cross-plane thermal conductivity with gas infiltration (left axis) and the decrease in gas diffusivities (right axis) for the three different COFs.
pathways in the cross-plane direction for 2D COFs. The important role played by gas diffusivities is also highlighted by our additional simulations on mass-perturbed methane/COF-5 systems, where varying the mass of the methane gas leads to changes in the diffusivities of the gas adsorbates and ultimately to the relative contributions from the guest and the host species to the overall cross-plane thermal conductivity (see Figure S12). In summary, our results show the inherent anisotropic nature of thermal transport in 2D COFs. This anisotropy can be manipulated with the addition of methane gas adsorbates at different gas densities. More specifically, as the methane gas density increases, the thermal conductivity along the direction of the lamellar pores increases due to additional heat transfer pathways. The thermal conductivity along the 2D sheets, however, decreases monotonically with increased gas density. We show that collisions between the methane gas and the solid framework give rise to additional channels of heat transfer along the lamellar pore channels. However, this additional “heat pathway” does not enhance heat transfer in the in-plane direction and rather leads to further scattering of vibrations along the layers, thereby reducing the thermal conductivity in the in-plane direction. Our atomistic simulations reveal that the thermal conductivity along the direction of the pore channels for methane-infiltrated COFs is directly related to the diffusivities of the gas molecules.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01863.

Details of the computational domain setup, equilibrium molecular dynamics approach, vibrational density of states calculations, heat flux calculations, and gas diffusivity calculations (PDF)

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Notes
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