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 ABSTRACT: UiO-67 metal–organic frameworks (MOFs) show promise for use in a variety of areas, especially in industrial chemistry, as stable and customizable catalyst materials often driven by catalytically active defects (coordinatively
 Image: CD₃CN Adsorption - CD₃CN Diffusion - CD

unsaturated metal sites) present within the MOF crystallite. Thermal activation, or postsynthetic thermal treatment, of MOFs is a seldom used method to induce catalytically active defects. To investigate the effect of thermal activation on defect concentration in UiO-67, we performed Fourier transform infrared (FT-IR) spectroscopy studies of adsorbed CD₃CN, a versatile infrared active probe molecule. Our results suggest that, under cryogenic, ultrahigh-vacuum conditions, CD₃CN must be thermally diffused into UiO-67 to successfully detect binding sites and defects. Below dehydroxylation temperatures, blueshifted ν (CN) modes



of diffused CD₃CN indicate multiple avenues of hydrogen bonding within UiO-67, as well as binding to Lewis acid sites, assigned to be coordinately undersaturated Zr⁴⁺, consistent with in situ FT-IR of adsorbed CO. FT-IR of CD₃CN diffused into UiO-67 activated to 623 K shows that while thermal activation eliminates hydrogen-bonding moieties, it also induces stronger Lewis acid sites, identified by a blueshifted ν (CN) doublet. Through density functional theory (DFT) calculations, we demonstrate that the ν (CN) doublet is a result of CD₃CN interacting with two distinct nodal defect sites present in dehydroxylated UiO-67. Additionally, the infrared cross sections of CD₃CN's ν (CN), ν (CD)_s and ν (CD)_{as} modes change, primarily due to hydrogen bonding, when diffused into UiO-67, as confirmed through DFT calculations. The nonlinear IR cross section behavior suggests that the Beer–Lambert law cannot trivially extrapolate the concentration of an analyte diffused into a MOF. These studies reveal the impact of postsynthetic thermal treatment on the concentration and type of Lewis acid defects in UiO-67 and caution the simple use of integrated infrared absorbance as a metric of analyte concentration within a MOF.

INTRODUCTION

Metal-organic frameworks (MOFs) are versatile porous materials that exhibit attractive properties, e.g., high surface areas and catalytic activity.^{1–3} MOFs can be tailored for targeted applications such as the degradation of chemical warfare agents and the capture of toxic industrial chemicals by tuning the coordinating ligands, metal, and defect concentration (e.g., open metal Lewis acid sites, missing linker sites).⁴⁻¹² Lewis acidity, a tunable attribute of MOFs, arises due to open metal defects and can determine the effective utilization and application of MOFs for catalysis. The UiO (University of Oslo) family of Zr MOFs are structurally sound due to strong Zr-OC bonds between the linker and the node.^{13,14} An ideal (defect-free) UiO-67 MOF comprises $Zr_6O_4(\mu_3-OH)_4$ nodes, which are 12-connected by bidentate biphenyldicarboxylate (BPDC) linkers, which results in the formation of a complex framework.¹ The hierarchical framework not only provides a large surface area for analyte sorption but also allows access to ample catalytic sites.¹⁵

The chemistry of defective UiO-67 is well reported.^{16–18} The most common type of defect in UiO-67 is the loss of

BPDC linkers, which may yield coordinatively unsaturated Zr⁴⁺ Lewis acid sites depending on the capping groups.^{19,20} Defect concentration is typically engineered via manipulating the temperature of MOF synthesis, modulator choice, and concentrations.²¹ Defects are unavoidable even in the most optimized MOF synthetic process and are suggested to be the locus of catalytic activity in MOFs.^{8,15,17,22–24} This catalytic activity is generally assigned to the increase in density of catalytic sites in a MOF and porosity,²¹ which enables the diffusion of reactants (and products) toward (and away from) active sites.

A primary focus of UiO-67 chemistry has been the identification and control of synthetic defects. Defects can also be introduced post synthesis via heating, i.e., temperature-

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induced defects. It has been reported that UiO-67 MOFs, under controlled ultra-high-vacuum (UHV) conditions, retain their mechanical stability until a temperature of ca. 700 K.²⁵ Dehydroxylation occurs by heating UiO-67 between ca. 500 and 600 K.^{22,25} It has additionally been reported that under ambient conditions, thermally activated UiO-66 MOFs have a higher density of defect sites.^{26,27} Since UiO-66 and UiO-67 share identical nodal structures and differ primarily by the identity of the linker molecule,²⁸ thermal activation of UiO-67 should show a similar response. It is thus of interest to identify the types and Lewis acidities of defects induced during the thermal activation of UiO-67 MOFs. To this end, a method sensitive to such defect sites, created through thermal activation of UiO-67 MOFs, must be employed.

Defect concentrations in UiO MOFs are typically quantified via thermogravimetric analysis (TGA) (Figure S1).^{25,29} Defects can also be characterized via a variety of methods, including X-ray diffraction, temperature-programmed desorption mass spectrometry (TPD-MS), in situ Fourier transform infrared (FT-IR) spectroscopy, temperature-programmed FT-IR (TP-IR).^{17,22,26,27,30} While defects and active sites are present on a MOF exterior, catalysis is largely dependent on internal sites and hence internal defects.³¹ Thus, characterization of the internal sites in porous MOFs is essential to obtain an understanding of the MOF defect concentration.

To understand internal MOF chemistry, probe molecules must be transported into the MOF crystallite to allow interaction with its internal sites.^{31,32} An ideal probe molecule should distribute itself among the various possible binding sites. CD₃CN is an effective infrared probe molecule used to elucidate the presence of hydroxyl groups and Lewis acid sites in metal oxides, zeolites, and MOFs, including UiO-66.^{26,33-36} A commonly used vibrational probe of chemical functionalities present on surfaces is CO.^{37,38} However, the multilayer desorption temperature of CO from graphene in the low coverage limit is ca. 50 K,³⁹ which is below the base temperature of our UHV systems (ca. 90 K). 40,41 The corresponding CD₃CN multilayer desorption temperature from graphene in the low coverage limit is ca. 150 K_{1}^{42} well above the base temperature of our UHV systems. Therefore, CD₃CN was chosen as a reasonable probe molecule to interpret how diffusion from an adsorbed external multilayer into the UiO-67 crystallite can provide insight into the chemical structure of internal MOF sites. The interaction of CD₃CN with catalytic sites in UiO-67, e.g., Zr⁴⁺ Lewis acid sites, can be determined from blue shifts in ν (CN), making it a useful infrared active probe molecule.³⁵

Analogously, a common method employed to probe analyte transport kinetics through porous materials is infrared spectroscopy.⁴³ These studies correlate integrated infrared intensity to analyte presence within a MOF.³² The key assumption is that an analyte diffused into a MOF obeys the Beer–Lambert law.^{32,44,45} However, there have been scenarios reported over the past 40 years which highlight the breakdown of the Beer–Lambert law for analytes adsorbed on metal surfaces and diffused into single-wall carbon nanotubes.^{37,46–50} Thus, it is important to determine whether a probe molecule obeys the Beer–Lambert law, especially if analyses based on infrared absorbance are employed.

To ensure that only CD_3CN -MOF interactions were investigated, i.e., to eliminate atmospheric contaminant interference, studies were performed under ultra-high vacuum (UHV) at cryogenic temperatures. To determine the binding

strength of CH₃CN to UiO-67, we employed TPD-MS. The impact of thermal treatment on defects in the interior (bulk) of the UiO-67 crystallite was evaluated spectroscopically via in situ FT-IR of isothermally diffused CD₃CN.⁵¹ Surprisingly, it is observed that the $\nu(CD)_{s}$, $\nu(CD)_{as}$ and $\nu(CN)$ modes of CD₃CN show disproportionate intensity behavior when diffused into UiO-67, that is, the Beer-Lambert law cannot quantify the concentration of CD₃CN present in UiO-67. This behavior arises due to changes in the infrared cross sections of these modes when CD₃CN hydrogen bonds to the μ_3 -OH groups. In situ FT-IR results indicate that thermal activation of UiO-67 decreases the concentration of OH groups and simultaneously induces the formation of Lewis acid sites, which appear to increase in both concentration and strength following dehydroxylation of the MOF. Our work shows the impact of thermal activation on defect strength and concentration and highlights the importance of probe molecule transport for revealing MOF properties. We highlight that even in a low coverage limit, the Beer-Lambert law is not always quantitatively reliable for probing the presence, or concentration, of molecules diffused into the MOF crystallite.

EXPERIMENTAL SECTION

The UiO-67 MOFs used herein were synthesized using a protocol described elsewhere.²⁹ Powder X-ray diffraction (PXRD) patterns were collected using a Bruker AXS D8 discover powder diffractometer at 40 kV and 40 mA for Cu K α (λ = 1.5406 Å) with a scan speed of 0.10 s/step from 3 to 35° at a step size of 0.02°. The data were analyzed by using the EVA program from the Bruker powder analysis software package. Thermogravimetric analyses (TGA) were performed using a TGA Q500 thermal analysis system under a nitrogen atmosphere from room temperature to 1073 K at a ramping rate of 2 K min⁻¹.

Acetonitrile (Sigma-Aldrich, suitable for HPLC, gradient grade, \geq 99.9%, CAS: 75-05-8) and acetonitrile- d_3 (Cambridge Isotope Laboratories, 99.8% D, CAS: 2206-26-0) were subjected to 3–5 consecutive freeze–pump–thaw cycles (Figures S3 and S4) as described elsewhere.³² CO (Airgas, CAS: 630-08-0) was used as obtained.

Temperature-programmed desorption mass spectrometry (TPD-MS) and Fourier transform infrared spectroscopy (TP-FT-IR) experiments were performed in previously described custom-built stainless steel ultra-high vacuum (UHV) chambers.^{40,41} The chambers achieved a pressure of $<1.0 \times 10^{-8}$ Torr following bakeout. Chamber pressures were monitored via a nude ion gauge (Duniway, Ir filament), controlled via an ion gauge controller (Granville Phillips 307), and recorded via custom routines in LabVIEW 14.0 software (National Instruments).

UiO-67 sample preparation is described in detail elsewhere.²⁹ Briefly, UiO-67 samples were dispersed in DMF and centrifuged. The resultant sample (ca. 2 mg) was slurry cast upon the center of an acetone-sonicated W grid (Alfa Aesar). A fast response K-type thermocouple (Omega) was spot-welded to the W grid which was braced to a Cu manipulator to provide rapid cooling (to ca. 100 K) and Joule heating, using direct current from a power supply (SCR 10-80, Electronic Measurements Inc.). Sample activation was performed from a base pressure <1.0 × 10⁻⁸ Torr by heating the UiO-67 samples at 473 K for 15 min, as described elsewhere.⁵¹ Thermal treatment to higher activation temperatures (T_{act}) was performed by heating the already activated MOF for 15 min at the desired T_{act} .

Acetonitrile doses were made by exposing the UiO-67 sample to a constant pressure of acetonitrile, typically 10^{-5} Torr, through a leak valve (Varian VLVE-2000). Exposures are reported in Langmuirs, L, where 1 L $\equiv 10^{-6}$ Torrs, and are calculated based upon uncorrected ion gauge readings.

For TPD-MS experiments, following acetonitrile exposure at ca. 100 K and once the chamber pressure recuperated to $<1.0 \times 10^{-8}$

Torr, the sample was heated at ca. 2 K s⁻¹ from ca. 100 K to T_{act} . Acetonitrile mass fragments m/z = 40 and 41 were tracked as a function of temperature using a shielded residual gas analyzer (Stanford Research Systems RGA 300) installed in the UHV chamber. CH₃CN was used in place of acetonitrile- d_3 (CD₃CN) for TPD-MS studies due to similar desorption profiles (Figures S5 and S6).⁴²

In situ Fourier transform infrared (FT-IR) spectroscopy was used to investigate the interaction of acetonitrile with MOF specific moieties in real-time via an FT-IR spectrometer (Bruker, Tensor 27). Spectra were recorded in transmission mode between 4000-400 cm⁻¹ at 4 cm⁻¹ resolution, with a room-temperature DLaTGS detector and averaged over 16 scans (6 mm aperture, 10 kHz scanning velocity). A 64-scan background spectrum of the bare W mesh at room temperature (ca. 295 K) was recorded and used as a reference prior to each experimental cycle. Spectra were baselinecorrected with OPUS 7.5 software with the following conditions: Concave Rubberband Correction (10 iterations), 256 baseline points, CO_2 bands excluded. We present the spectra of UiO-67 ($T_{act} = 473$ K) and UiO-67 (T_{act} = 623 K), as shown in Figures 3 and 6, respectively, prior to baseline correction in Figures S25 and S26, respectively. The quantitative results showing the presence of $\nu(CN)_{HB}$ and the lack of $\nu(CD)_{as}$ are consistent with the baselinecorrected spectra (Figure 3).

Isothermal diffusion experiments follow a method similar to typical adsorption—desorption experiments.⁴⁹ The hold temperature (T_{hold}) was chosen such that weakly physisorbed species were removed from the MOF, while strongly adsorbed molecules diffused in. Specifically, T_{hold} is either 170 K, less than the desorption temperature of strongly bound acetonitrile, 199 K (Figure 1), or 130 K, less than the onset desorption temperature of weakly bound acetonitrile (ca. 150 K). After adsorption at 100 K, and once the chamber pressure recuperated to ca. < 5.0×10^{-8} Torr, the sample was resistively heated to the hold temperature of choice, T_{hold} , at 0.5 K s⁻¹, while infrared spectra are taken continuously. Once the sample temperature reached T_{hold} , the temperature was held constant for 60 min and then the sample was allowed to cool. Once the sample temperature stabilized (typically, ca. 100 K), the sample was heated to the desired activation temperature at a rate of 1 K s⁻¹.

The binding configuration and energy of acetonitrile to UiO-67 were investigated using ab initio molecular dynamics (AIMD) simulations, described in more detail elsewhere.²⁹ Briefly, periodic density functional theory (DFT) calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional⁵³ with Goedecker-Teter-Hutter pseudopotentials⁵⁴ and the DZVP-MOLOPT-SR basis set,⁵⁵ including Grimme's D3 dispersion correction,⁵⁶ in CP2K.⁵⁷⁻ The atom positions of the UiO-67 primitive cell, using lattice parameters a = b = c = 19.1 Å, $\alpha = \beta = \gamma = 60^{\circ}$, were relaxed using DFT in CP2K. The conjugate gradient orbital transformation minimizer was used.⁶⁰ Two sets of simulations in the canonical (NVT) ensemble using the Nose-Hoover thermostat⁶¹ were run for 5 ps with a time step of 1.0 fs. The coordinates of the simulations were sampled every 100 fs and relaxed to their local minima. The first simulation was run at 500 K to enable sampling of many different configurations. The minimum energy structure identified from the first simulation was used as the starting point for the second simulation, where the temperature was set at 300 K to explore configurations in the neighborhood of the minimum energy structures. The resultant relaxed structures were used to calculate binding energies, ΔE_{bind} , defined as

$$\Delta E_{\rm bind} = E_{\rm MOF+\,analyte} - E_{\rm MOF} - E_{\rm analyte} \tag{1}$$

where $E_{\text{MOF}+\text{analyte}}$ is the total energy of the MOF with acetonitrile, E_{MOF} is the energy of the empty MOF, relaxed to its ground state, and E_{analyte} is the energy of relaxed acetonitrile in the gas phase. For the computational IR spectra of CD₃CN and the defect-free hydroxylated CD₃CN-Zr₆O₄(μ_3 -OH)₄(HCOO)₁₂ cluster, the harmonic vibrational frequencies were calculated at the B3LYP/6-31+G(d) level of theory with D3 dispersion corrections using the Gaussian 16 package. ^{56,62–66} The B3LYP density functional has provided satisfactory results in previous computational studies of acetonitrile and is thus employed in this current study. 67

We have developed cluster models of the secondary building unit (SBU) to facilitate calculations of the FT-IR spectra of the acetonitrile binding to defect-free and defective (missing linkers) UiO-67. All of these SBU clusters were optimized with the B3LYP level of theory with D3 dispersion corrections. The structures do not have negative frequencies. The 6-31+G(d) basis set was selected for C, O, N, and H atoms, and the Los Alamos National Laboratory double Zeta (LANL2DZ) and triple Zeta (LANL2TZ) basis sets were used with the relativistic effective core potentials for Zr.⁶⁸

RESULTS AND DISCUSSION

TPD-MS. To characterize the binding of acetonitrile to UiO-67, TPD-MS studies were performed. We choose acetonitrile exposures of ca. 1000 L so that the resultant spectrum is in the low coverage limit. Note that the exposure unit, Langmuir (L), is defined as $1 L \equiv 1 \times 10^{-6}$ Torr·s. A complete CH₃CN monolayer on the MOF is equivalent to a CH₃CN exposure of approximately 50,000 L for the sample sizes used in these investigations. Therefore, if the CH₃CN molecules distributed themselves throughout the MOF crystallite, 1000 L of CH₃CN exposure results in a coverage of roughly 2% (see the Supporting Information for more details). Since it has been previously reported that acetonitrile does not have an observable interaction with UiO-67,⁶⁹ it is important to understand if acetonitrile interacts with MOF specific moieties or simply adsorbs as a multilayer.

The desorption profile of 1000 L of acetonitrile from UiO-67 ($T_{act} = 473$ K) reveals a low-temperature feature and a broad, asymmetric higher-temperature feature (Figure 1). The shape and temperature of the low-temperature feature is suggestive of multilayer desorption, while the latter feature is suggestive of interaction with UiO-67 MOF moieties.^{42,70,71} We note that the low-temperature feature is likely a convolution of multilayer desorption and weakly bound CH₃CN desorption from the MOF.



Figure 1. TPD-MS spectrum tracking the partial pressure of acetonitrile mass fragment m/z = 41 while heating UiO-67 ($T_{act} = 473$ K) from ca. 113 to 473 K following 1000 L CH₃CN exposure. The heating rate (β) is ca. 2 K s⁻¹.

The experimental molar desorption activation energy, $E_{\rm des}$, for acetonitrile interacting with UiO-67 is computed via Redhead analysis.^{40,72} Due to the asymmetry of the high-temperature peak,⁴⁰ first-order desorption is assumed. The Redhead equation (eq 2) shows that $E_{\rm des}$ of a first-order desorption process can be approximated as

where *R* is the ideal gas constant (8.314 J mol⁻¹ K⁻¹), $T_{\rm m}$ is the temperature of maximum desorption of the experimental TPD-MS trace, ν is the pre-exponential factor (in s⁻¹), and β is the heating rate (ca. 2 K s⁻¹).⁷² While transition state theory shows translational, rotational, and vibrational partition functions are present in the definition of ν , their contributions are often ignored, which yields the typically used value of $\nu \sim 10^{13}$ s⁻¹.^{73–76} However, as calculated and discussed by Kay et al., we choose $\nu = 10^{16}$ s⁻¹ due to a non-negligible rotational contribution to ν at low temperatures for CH₃CN.⁴²

Redhead analysis of the high-temperature feature shows that CH₃CN interacts with UiO-67 (T_{act} = 473 K) with E_{des} = 63.8 ± 1.4 kJ/mol at 1000 L exposure. Compared to the reported value of CH₃CN multilayer desorption, ca. 49 kJ/mol,⁷⁷ this indicates non-negligible MOF-acetonitrile interactions and is consistent with values for monolayer CH₃CN desorption from Pt(111).^{42,77} The broad profile for the high-temperature feature suggests two possibilities: multiple acetonitrile binding sites with similar binding energies present on UiO-67, or diffusion-limited desorption. If acetonitrile diffuses into UiO-67 during the temperature ramp, its exit will be hindered by hydrogen bonding with hydroxyl groups and short-range interactions with other UiO-67 moieties.⁴⁴ Our periodic density functional theory (DFT) calculations show that CH₃CN hydrogen bonds to a UiO-67 μ_3 -OH group with an interaction energy of ca. 53 kJ/mol (Figure S7), consistent with the proposed hypothesis that CH₃CN hydrogen bonds to internal MOF moieties before desorption. Therefore, we presume that acetonitrile permeates the MOF membrane during heating. Hence, acetonitrile is proposed to be a reasonable candidate for probing the effect of thermal activation on UiO-67. To complement the insight determined from TPD-MS, we turned to vibrational spectroscopy to identify and understand the origin of these intermolecular interactions.

Infrared Spectroscopy. CD₃CN is an ideal molecule for vibrational spectroscopic analyses because of the features that appear in its infrared spectrum upon interaction with complex materials.³⁰ Due to the sensitivity of CD₃CN's ν (CN) stretch to the acidity of Zr⁴⁺ and OH groups, these features can elucidated through a blueshift in ν (CN).^{34,35} CD₃CN is also known for inducing intense, broad ν (OH) features through interaction with surface hydroxyl groups, providing a marker for the effect of thermal activation on changes to the MOF chemical characteristics.^{30,34}

CD₃CN is used in place of CH₃CN because the CN stretching region in the infrared spectrum of CH₃CN is complicated by a Fermi resonance which mixes the C==N stretch, ν (CN) and a combination mode of the C–C stretch (ν (CC)) and CH₃ symmetric bend (δ (CH)_s), i.e., ν (CC) + δ (CH)_s.^{33,78} Detailed discussions regarding the spectral implications of a Fermi resonance can be found elsewhere.^{33,79,80} The substitution of deuterium in place of hydrogen lifts the near-degeneracy of ν (CN) and ν (CC) + δ (CH)_s so that the CN stretching region is simplified to a single feature in neat CD₃CN.⁸⁰

As discussed, CD_3CN has been adsorbed on various MOFs (including UiO-66) to characterize possible defect sites.^{26,30} Thus, to substantiate conclusions drawn from the TPD-MS

spectrum (Figure 1), CD₃CN was adsorbed on UiO-67 (T_{act} = 473 K) at 100 K for IR studies. The full IR spectra prior to and following CD₃CN exposure at all of the different T_{act} 's in this study are presented in Figures S8–S12 and S13–S17, respectively. Note that the bands present in the spectrum in the 2200–2300 cm⁻¹ region prior to CD₃CN exposure are unidentified, intrinsic UiO-67 framework modes. Following activation at 473 K, the infrared spectrum of UiO-67 in the 3200–3500 cm⁻¹ region is void of signal, suggesting successful removal of any residual solvent from the MOF, or that any modes in the 3200–3500 cm⁻¹ region will be due to CD₃CN-MOF interactions. Upon exposure to UiO-67 (T_{act} = 473 K) at 100 K, features related to condensed phase CD₃CN: ν (CD)_{as}, ν (CN) at 2113, 2251, and 2261 cm⁻¹, respectively, are observed (Figure 2).^{78,81} This is in contrast to previous



Figure 2. FT-IR spectra of UiO-67 ($T_{act} = 473$ K) in (a) 3800–3200 cm⁻¹ and 2350–2100 cm⁻¹ regions. Black trace = Prior to adsorption, red trace = 2500 L CD₃CN exposure, blue trace = after desorption. The before adsorption and after desorption traces largely overlap, so most changes are indistinguishable. All spectra are taken at 100 K and baseline-corrected.

results performed under ambient conditions, which suggested acetonitrile does not adsorb to UiO-67.⁶⁹ Bands of relatively small intensity at ca. 2200 and 2220 cm⁻¹ are present likely due to the presence of ¹³C isotopic analogues of CD₃CN.⁸⁰ Relevant band identifications are summarized in the Supporting Information (Table S2). Successful CD₃CN adsorption upon UiO-67 thus provides us the ability to use it as an infrared active probe molecule of UiO-67 moieties.

To distinguish between modes perturbed due to interactions of CD₃CN with UiO-67 moieties, the mode associated with the CN stretch of bulk (multilayer) CD₃CN is labeled as ν (CN)_{bulk}. A band with a small intensity at 2301 cm⁻¹, suggestive of ν (CN)_{LA}, where CD₃CN interacts with open metal Zr⁴⁺ sites, indicates the presence of Lewis acidic Zr⁴⁺ groups.^{26,30} The mode at 2301 cm⁻¹ suggests that activation to 473 K results in the creation of Lewis acid catalytic sites or that they were present following synthesis. Indeed, our TGA data (Figure S1) suggest, on average, the presence of ~1.5 linker defects, which likely result in the mode at 2301 cm⁻¹. Modes present in the 3250–3370 cm⁻¹ region are due to combination modes of CD₃CN.⁷⁸ The observation of a broad band centered at ca. 3430 cm⁻¹ (Figure 2) depicts CD₃CN hydrogen bonding with hydroxyl groups present on UiO-67, consistent with the small decrease in ν (OH)_{free} intensity (Figure S18).³⁴

Despite the presence of the band at 3430 cm^{-1} indicative of CD₃CN hydrogen bonding with free hydroxyl groups, the



Figure 3. TP-IR spectra acquired during heating UiO-67 (T_{act} = 473 K) from (a) 100 K (dark blue) to 170 K (green) and from (b) 170 K (green) to 473 K (dark red) at ca. 0.5 K s⁻¹ following 2500 L CD₃CN exposure at 100 K. Black trace is prior to adsorption (i.e., clean MOF); Black and dark blue spectra were taken at 100 K.



Figure 4. FT-IR spectra of UiO-67 (T_{act} = 473, 523, 573 K) in (a) 3740–3620 cm⁻¹, (b) 2340–2270 cm⁻¹, and (c) 2270–2100 cm⁻¹ regions. Black trace = prior to adsorption, red trace = 2500 L CD₃CN adsorption; purple trace = following 60 min hold at 170 K. The postdesorption traces are removed for clarity, as they overlap with the black trace, but are presented in the SI. All spectra are taken at 100 K and baseline-corrected.

expected blueshift in ν (CN) at ca. 2280–2300 cm⁻¹, ν (CN)_{HB}, corresponding to the hydrogen-bonded CN stretch mode,⁸² was not seen. The absence of these bands suggests the ν (OH)_{HB} transition dipole is significantly larger than that of ν (CN)_{HB}, consistent with previous literature results for low concentrations of CH₃CN in H₂O.⁸³ It is thus concluded that upon exposure at 100 K, there is minimal CD₃CN access to MOF moieties, i.e., CD₃CN is primarily adsorbed as a multilayer on the external surface and barely permeated into the crystallite.

During sample heating to 473 K following CD₃CN adsorption TP-IR shows the emergence of a band at ca. 2280 cm⁻¹ (Figure 3). This spectral feature suggests that CD₃CN diffuses into UiO-67 and probes internal hydroxyl groups during heating, consistent with the TPD spectrum (Figure 1). Since we presume that ν (CN)_{bulk} is indicative of multilayer CD₃CN, its absence, coupled with the presence of ν (CN)_{HB} ca. 2280 cm⁻¹, shows CD₃CN has successfully permeated the MOF crystallite and is preferentially interacting with MOF moieties. Hence, temperature-induced mass transport of CD₃CN into UiO-67 is required to probe the internal sites under cryogenic UHV conditions.

To promote CD_3CN transport into UiO-67, following exposure at 100 K, the sample was heated to 170 at 0.5 K s⁻¹, then held at 170 K for 60 min, and then cooled back to 100 K. This facilitates multilayer removal and promotes the inward

diffusion of physisorbed CD₃CN molecules.⁵¹ The methodology employed here is similar to that of Kazachkin et al. to remove weakly adsorbed species from single-wall carbon nanotubes.⁴⁹ The hold temperatures (T_{hold}) were chosen to maximize multilayer desorption and simultaneously minimize strongly physisorbed CD₃CN desorption, guided by the maximum desorption temperatures in the TPD-MS spectrum (Figure 1). See the Supporting Information for more details. Following the hold, the sample was immediately cooled back to 100 K and CD₃CN–UiO-67 features become more apparent (Figure 4), which suggests that CD₃CN successfully diffused into UiO-67 to interact with internal moieties, i.e., moieties not present on the external crystallite.

The doublet at 2280 and 2289 cm⁻¹ (Figure 4b) on UiO-67 ($T_{act} = 473$ K) suggests hydrogen-bonding interactions following diffusion into UiO-67. These bands were likely convoluted in the feature identified as ν (CN)_{HB} in Figure 3. The band at 2280 cm⁻¹, due to hydrogen bonding between CD₃CN and the μ_3 -OH group, mimics the behavior of CD₃CN interactions with Brønsted acid sites on ZrO₂.⁸² The intensity increase and spectral broadening in ν (OH)_{HB} at 3430 cm⁻¹ following the 60 min hold at 170 K further supports this assignment (Figure S14).³⁴ The band at 2289 cm⁻¹ is consistent with a perturbed ν (CN) of CD₃CN adsorbed on zeolites.⁸⁴ The intensity of the mode at 2301 cm⁻¹ following the hold at 170 K is nearly identical to that prior to the hold

(Figures 2 and 4b). The lack of intensity change suggests that at T_{act} = 473 K, UiO-67 has a few fully dehydroxylated Lewis acid sites present.

The presence of $\nu(OH)_{free}$ at 3678 cm⁻¹ is an indicator of MOF integrity, as changes to its intensity can report on analyte binding or dehydroxylation.^{26,30} Interestingly, there is an apparent blueshift in $\nu(OH)_{\text{free}}$ to 3680 cm⁻¹ (Figure 4a) following the hold at 170 K. This is ascribed to a weakening of the Zr-OH bond. See the Supporting Information for more details. It has been shown under high-vacuum conditions that adsorbed CD₃CN is capable of displacing H₂O molecules on ZrO₂.⁸² To determine if this process occurs, we compare the line shape of $\nu(OH)_{free}$ before, during, and after CD_3CN exposure (Figure S18). The ν (OH)_{free} line shape, reported to be a combination of both μ_3 -OH and isolated H_2O species,^{22,30} is initially symmetric and becomes slightly asymmetric following CD₃CN desorption (blue trace, Figure S18). The induced asymmetry suggests that CD₃CN successfully displacing a small fraction of H₂O ligands. Therefore, after $\mathrm{CD}_3\mathrm{CN}$ is desorbed, undercoordinated Zr^{4+} sites are likely present in the MOF due to the loss of H₂O ligands. Nonetheless, the intensity of $\nu(OH)_{\rm free}$ nearly restores to its maximal intensity following CD₃CN desorption at all activation temperatures prior to dehydroxylation. While CD₃CN appears to induce some structural change to UiO-67 through the removal of H_2O ligands, there is little asymmetry in the $\nu(OH)_{free}$ following desorption, which still makes CD₃CN a viable infrared probe for interpreting temperatureinduced chemical changes in UiO-67.

A puzzling aspect of the IR spectra is the disappearance of both $\nu(CD)_{as}$ and $\nu(CD)_{s}$ during the temperature ramp, despite CD₃CN remaining in the MOF, indicated by the presence of $\nu(CN)_{\rm HB}$ at ca. 2280 cm⁻¹ (Figures 3 and 4). The intensity of the $\nu(CD)$ modes when CD₃CN is initially adsorbed on UiO-67 at 100 K is consistent with previous infrared studies of solid CD₃CN.^{81,85} This $\nu(CD)$ intensity loss phenomenon has been seen in both the $\nu(CD)_{as}$ and $\nu(CD)_{s}$ modes in CD₃CN adsorbed on acidic zeolites, CD₃CN in solution, and CD₃CN:EtOH, CD₃CN:H₂O ices.^{86–92} It appears that as CD₃CN hydrogen bonds with OH groups, the $\nu(CD)$ mode intensities decrease while the $\nu(CN)_{\rm HB}$ mode intensity increases. Therefore, the loss of intensity in both $\nu(CD)$ modes suggests that, alongside the growth of $\nu(CN)_{\rm HB}$, CD₃CN successfully diffuses into UiO-67.

Typically, the intensities of infrared features can be used as a probe of analyte concentration, assuming Beer–Lambert's law.⁹³ Such an approximation is usually reasonable in the limit of small analyte coverage, but there are known instances where infrared absorbance has a nonlinear dependence on analyte concentration.^{46–48} Specifically here, one should expect the integrated intensity of the ν (CD) modes to remain proportional to the integrated intensity of the ν (CD) modes. However, there is clear disproportionate, nonlinear behavior in the intensities of the ν (CD)_s, ν (CD)_{as} modes (red and orange traces, Figure 5) compared to the total integrated intensity of the ν (CN) modes. Figure 5).

Correlation traces (Figures S22–S24) suggest a nonlinear relationship between the integrated intensities of ν (CD)_s and ν (CD)_{as}, ν (CD)_s and ν (CN)_{HB} + ν (CN)_{LA} between ca. 165–205 K. During heating, infrared modes intrinsic to a clean UiO-67 sample (i.e., no analyte adsorbed) in the 2200–2300 cm⁻¹ region decrease slightly in intensity (Figure S12). Thus,



Figure 5. Integrated absorbance of $\nu(CN)_{bulk}$ (purple, circles), $\nu(CN)_{HB} + \nu(CN)_{LA}$ (yellow, triangles), $\nu(CD)_{as}$ (orange, squares), and $\nu(CD)_s$ (red, diamonds) as shown in Figure 3 during flash heat. Nonzero backgrounds are present due to intrinsic MOF IR modes in the 2100–2300 cm⁻¹ region. The maximum $\nu(CN)_{HB} + \nu(CN)_{LA}$ integrated absorbance is reached at ca. 170 K.

increases in the integrated infrared intensities (Figure 5) are purely from CD₃CN-MOF interactions. Specifically, when hydrogen-bonded CD₃CN molecules desorb from UiO-67, as determined by a loss in the infrared intensity of the ν (CN)_{HB} + $\nu(CN)_{LA}$ mode (yellow trace, Figure 5), there is little change in the integrated $\nu(CD)$ intensities (orange and red traces, Figure 5). Note that this phenomenon is observed following the diffusion of CD_3CN into UiO-67 (purple traces, Figure 4). This behavior appears similar to infrared studies of acetone molecules diffused into carbon nanotubes as well as CO adsorbed on metal surfaces.^{37,46–49} This nonlinear ν (CD) intensity behavior shows that these modes cannot be used trivially as a metric of the quantity of CD₃CN present in UiO-67. This cautions the use of integrated infrared absorbance as a probe of analyte presence in the MOF crystallite, which is often used to quantitatively evaluate the kinetics of molecular diffusion out of the MOF.

To effectively simulate binding of CD₃CN to a μ_3 -OH group, we performed calculations of CD₃CN interacting with a hydroxylated SBU cluster. We found that the simulated infrared spectrum of the cluster shows a significant decrease in the relative intensity of the ν (CD) modes. The calculated IR spectrum for the optimized $CD_3CN-Zr_6O_4(\mu_3 OH)_4(HCOO)_{12}$ cluster (Figure S27) shows an intensity decrease in both $\nu(CD)_{s}$, $\nu(CD)_{as}$ as compared to that of a corresponding calculated CD₃CN infrared spectrum. Based on the analysis of the spatial dipole derivative with respect to one of the doubly degenerate $\nu(CD)_{as}$ modes, $^{94}\frac{\partial \vec{\mu}}{\partial Q}$, we found that the derivative of the dipole moment in the z direction is significantly reduced when CD₃CN is hydrogen-bonded (Table S6). This decrease leads to a significant reduction in the IR intensity, $I_{\rm IR}$ for $\nu(\rm CD)_{as}$ since $I_{\rm IR} \approx \left| \frac{\partial \vec{\mu}}{\partial Q} \right|^2$ under the electric dipole and harmonic approximations, where $\vec{\mu}$ is the molecular electric dipole moment and Q is the ν (CD)_{as} normal mode coordinate.⁹⁵ The calculated decrease in $I_{\rm IR}$ explains the experimental observation for the disappearance of $\nu(CD)_{as}$ despite CD₃CN remaining in the MOF.

The spectral changes induced by CD_3CN diffusion into the MOF allow for the characterization of the material. Hence,



Figure 6. FT-IR spectra of UiO-67 (T_{act} = 573, 623 K) in (a) 3740–3620 cm⁻¹, (b) 2335–2270 cm⁻¹, and (c) 2270–2100 cm⁻¹ regions. Black trace = prior to adsorption, red trace = 2500 L CD₃CN adsorption; purple trace = following 60 min hold at 130 K. All spectra are taken at 100 K and baseline-corrected.

perturbations in the infrared spectra following analyte diffusion will be insightful for understanding the impact of thermal activation on the chemical properties of UiO-67. We heated the samples to successively higher temperatures (473, 523, 573, 623 K) to probe the effect of thermal activation on structural and chemical properties of UiO-67.^{22,25} Upon thermal treatment to 523 and 573 K, changes in the spectra of UiO-67 are clear prior to CD₃CN adsorption: partial dehydroxylation of UiO-67, noted by the loss of the intensity in ν (OH)_{free} (black spectra, Figure 4a), consistent with previous studies.²⁶ With fewer free OH groups, due to thermal treatment, diffusion of CD₃CN into UiO-67 ($T_{act} = 523$, 573 K) at 170 K results in a decreasing total ν (CN)_{HB} intensity, consistent with the loss of ν (OH)_{free} intensity.

Following diffusion of CD₃CN into UiO-67 (T_{act} = 573 K) at 170 K, it appeared that a relatively small amount of CD₃CN remained, relative to T_{act} = 473 and 523 K (Figure 4). Since diffusion and desorption are temperature-activated processes, this implies that $T_{\text{hold}} = 170$ K increases the rate of desorption considerably for UiO-67 (T_{act} = 573 K). The loss of CD₃CN at $T_{\rm hold}$ = 170 K is consistent with the hypothesis that the hightemperature-binding feature observed in TPD at ca. 200 K appears to be due to hydrogen bonding between CH3CN and MOF moieties. Thus, since UiO-67 has been largely dehydroxylated by $T_{\rm act}$ = 573 K, a lower hold temperature should be chosen such that CD₃CN diffusion is favored over desorption. Based upon the TPD-MS spectrum (Figure 1), a temperature that minimizes CD₃CN desorption must be less than 150 K. Hence, to investigate the internal structure and Lewis acidity of UiO-67 activated to higher temperatures, 2500 L of CD₃CN is adsorbed and slowly diffused at a lower $T_{\rm hold}$, 130 K.

To determine if new Lewis acid sites exist at 573 K activation, CD_3CN was diffused into UiO-67 at a temperature of 130 K, reducing CD_3CN desorption compared to that at 170 K. The resultant spectra (Figure 6b) show a doublet following the hold, with bands present at 2301 and 2311 cm⁻¹. CO adsorption experiments on UiO-67 ($T_{act} = 573$ K) (Figure S19) are similar to those of Morris et al. on thermally activated UiO-66, which suggest dehydroxylation yields a growth in Zr^{4+} concentration,³⁸ consistent with our CD₃CN results. Therefore, activation to 573 K appears to induce sites of different Lewis acidities in UiO-67.

Based upon the behavior of CD₃CN diffused into UiO-67 ($T_{act} = 573$ K), we hypothesized that thermal activation at higher temperatures, dehydroxylating the MOF further, should induce an increase in the intensities of the doublet peaks at 2301, 2311 cm⁻¹. Upon thermal activation of UiO-67 at 623 K, the FT-IR spectrum (Figures 6 and S11) shows changes in several intrinsic motifs of the MOF. In particular, the complete loss of ν (OH)_{free} suggests that the MOF has been fully dehydroxylated, consistent with other studies.²⁵ Since CD₃CN is sensitive to the types of defects present in UiO-67, the effect of total dehydroxylation on the concentration of Lewis acid defects in thermally activated UiO-67 can be properly understood.

Following CD₃CN adsorption on UiO-67 (T_{act} = 623 K) at 100 K, a band at 2301 cm^{-1} is observed (Figure 6b). We assign this to internal Zr⁴⁺ sites as a result of CD₃CN diffusion into the MOF at 100 K. Following the hold at 130 K, a doublet $\nu(\text{CN})_{\text{LA}}$ feature at 2301, 2311 cm⁻¹ appears, but with a larger intensity than seen at $T_{act} = 573$ K (Figure 6b). For lower activation temperatures, no such doublet exists (Figure 4b). Recall that blueshifts of ca. 40-50 cm⁻¹ from ν (CN)_{bulk} suggest successful coordination of CD₃CN to a Lewis acid site.²⁶ The emergence of this $\nu(CN)_{LA}$ doublet (Figure 6) suggests that thermal activation of UiO-67 to its dehydroxylation onset temperature results in the creation of stronger Lewis acid sites relative to the Zr4+ coordinatively undersaturated sites. The increase in the intensity of this doublet suggests a growth in the concentration of Lewis acid sites within UiO-67 due to thermal activation. To identify the origin of the band at 2311 cm⁻¹, the spectra were compared to acetonitrile adsorption on zirconia (ZrO₂), which shares some chemical similarity to the UiO-67 node.25 However, FT-IR analysis of CD₃CN adsorbed upon ZrO₂ shows, to our knowledge, a maximum $\nu(CN)_{LA}$ frequency of 2306 cm^{-1,96} Thus, a different chemical species is responsible for this feature at 2311 cm⁻¹.

When UiO-67 is heated to 623 K, it is dehydroxylated, initiating a change of the node structure into a distorted Zr_6O_6 cluster.¹⁴ Zr_6O_6 is hypothesized to have chemical resemblance to tetragonal $\text{Zr}O_2$ (t- $\text{Zr}O_2$).^{97,98} However, the maximum $\nu(\text{CN})_{\text{LA}}$ frequency for CD₃CN adsorbed on t- $\text{Zr}O_2$ was reported to be ca. 2300 cm⁻¹,⁸² less than the maximum $\nu(\text{CN})_{\text{LA}}$ frequency, 2306 cm⁻¹, for CD₃CN adsorbed on any $\text{Zr}O_2$ species, to our knowledge.⁹⁶ Therefore, the spectra

Table 1. Calculated Binding Energies of CH₃CN and Vibrational (Harmonic) Frequencies of ν (CN) in the Gas Phase and Bound to Each of the Clusters in Figure 7, Computed at the B3LYP+D3/6-31+G(d)/LANL2DZ Level of Theory^{*a*}

| cluster SBU models | E _{bind} (kJ/mol) | Zr CN | unscaled $\nu({ m CN})~({ m cm}^{-1})$ | scaled $\nu({ m CN})~({ m cm}^{-1})$ | exp. (cm^{-1}) | |
|--|----------------------------|-------|--|--------------------------------------|------------------|----------------------------------|
| free CH ₃ CN | | | 2365 | 2261 | 2261 | $\nu(CN)_{bulk}$ |
| (a) $CH_3CN-Zr_6O_4(\mu_3-OH)_4(HCOO)_{12}$ | -36.47 | 8 | 2384 | 2280 | 2280 | $\nu(\mathrm{CN})_{\mathrm{HB}}$ |
| (b) $CH_3CN-Zr_6O_6(HCOO)_{12}$ | -32.04 | 8 | 2408 | 2303 | 2301 | $\nu(CN)_{LA}$ |
| (c) $CH_3CN-Zr_6O_4(\mu_3-OH)_4(\mu_1-OH)$ (HCOO) ₁₁ | -81.26 | 8 | 2401 | 2295 | N.O. | $\nu(CN)_{LA}$ |
| (d) CH ₃ CN-Zr ₆ O ₆ (μ_1 -OH)(HCOO) ₁₁ | -96.31 | 7 | 2392 | 2287 | N.O. | $ u(CN)_{LA} $ |
| (e) CH_3CN - $Zr_6O_7(HCOO)_{10}$ | -89.90 | 6 | 2408 | 2302 | 2301 | $\nu(CN)_{LA}$ |
| (f) $CH_3CN-Zr_6O_8(HCOO)_8$ | -57.81 | 8 | 2412 | 2306 | 2311 | $ u(CN)_{LA} $ |

^aThe identifiers (a), (b), etc. refer to Figure 7. Zr CN is the coordination number of the Zr atom to which acetonitrile is bound. The unscaled frequencies are the raw output from the DFT calculations. The scaled frequencies use a scaling factor of 0.956 to bring the calculated value of ν (CN)_{bulk} into agreement with the experimental value. Experimental frequencies for the observed species (Figures 4 and 6) are also shown. N.O. = not observed.



Figure 7. Optimized structures binding with CH₃CN for the different SBU clusters computed at the B3LYP+D3/6-31+G(d)/LANL2DZ level of theory. The yellow balls indicate μ_3 -OH and μ_1 -OH group hydrogens. Cluster (a) depicts binding of acetonitrile to pristine UiO-67 through the μ_3 -OH group. Cluster (b) shows binding to a Zr site by displacement of one of the formate bonds, as one could expect from a formate-capped missing linker defect in the MOF. Clusters (c)-(f) show how acetonitrile may bind to synthetically or thermally generated missing linker defects.

(Figure 6) suggest that dehydroxylated UiO-67 contains multiple types of Lewis acid sites, some of which can be stronger than those found in their metal oxide counterparts. This is consistent with recent results highlighting the impact of thermal treatment on UiO-66.²⁷ Note that an activation temperature of 623 K is ca. 250 K less than the decarboxylation temperature in UiO-67,²⁵ which can result in the presence of multiple Zr sites of differing coordination.

Importantly, the infrared spectra suggest that a distorted Zr_6O_6 cluster has a greater Lewis acidity than ZrO_2 . These results are consistent with a recent study studying the impact of thermal activation on the presence of Lewis acid defects in UiO-66.²⁷ Peng et al. noted that, at higher activation temperatures, the coordination number of the node decreases and forces the Zr atoms closer together, in agreement with the structure of dehydroxylated UiO-66 proposed by Valenzano et al.^{14,27} Our DFT calculations (vide infra) indicate that the two ν (CN)_{LA} modes at 2301, 2311 cm⁻¹ correspond to CD₃CN adsorbed upon dehydroxylated UiO-67 Zr sites having lower coordination number (Table 1). Hence, our results indicate that thermal activation is a feasible method for inducing sites of different Lewis acidities.

We have developed cluster models of the secondary building unit (SBU) to facilitate calculations of the FT-IR spectra of the acetonitrile binding to defect-free and defective (missing linkers) UiO-67. The generating processes for these cluster models are described in the SI, and the structures are shown in Figures S29 and S30. The binding configurations of acetonitrile (CH₃CN) to these clusters were generated by hand and optimized at the B3LYP+D3/6-31+G(d) level of theory followed by frequency calculations. Figure 7 shows the optimized SBU clusters binding with CH₃CN.

In Figure 7a, we show CH₃CN binding with μ_3 -OH on hydroxylated $Zr_6O_4(\mu_3-OH)_4(HCOO)_{12}$. For the dehydroxylated and defected SBU clusters, the Zr⁴⁺ Lewis acid sites coordinate with CH₃CN. Table 1 shows the binding energies of CH₃CN with the SBU clusters and the frequencies of the C≡N stretch modes for each of the SBU clusters and gas phase acetonitrile. It is instructive to compare the relative binding strengths of acetonitrile to each of the model SBUs. Cluster (d) exhibits the strongest binding energy due to the bidentate binding of CH₃CN to the SBU. The N atom binds to an open metal Zr site and one of the H atoms on CH₃CN hydrogen with the μ_1 -OH. The next strongest binding is to cluster (e), which has two missing linkers, with the N atom binding to a doubly undercoordinated Zr site. The next strongest binding energy is for cluster (c), which is missing one linker from the hydroxylated SBU model (a) by removing a carboxylate linker and capping with an OH group, following early work from Yaghi and co-workers.⁹⁹ The next strongest

binding energy is for cluster (f), which has four missing linkers. It has a smaller binding energy than cluster (e) because the added O atoms in (f) give higher coordination than those in (e). CH₃CN hydrogen-bonded to the μ_3 -OH group of the fully hydroxylated SBU has next to the lowest binding energy. Finally, CH₃CN bound to SBU (b), the dehydroxylated cluster, is the weakest even though it binds to a Zr metal site. The weak binding energy reflects the energy penalty of CH₃CN displacing formate binding to the Zr atom.

We also report computed vibrational frequencies for $\nu(CN)$ in Table 1. It is well known that harmonic approximation DFT calculated frequencies can overpredict experimental frequencies.⁶⁷ Hence, it is very common to apply a scaling factor to facilitate a direct comparison with experiments. We apply a scaling factor of 0.956 in order to make our calculated gas phase $\nu(CN)_{Bulk}$ frequency match experiments. We see from Table 1 that the scaled $\nu(CN)_{HB}$ of 2280 cm⁻¹ likely corresponds to CH₃CN binding with the μ_3 -OH in hydroxylated UiO-67, as seen by the good (perhaps fortuitous) agreement with the experiment. When CH₃CN binds to the Lewis acidic Zr⁴⁺ in the defective dehydroxylated SBU clusters, (e) and (f) of Table 1, the C \equiv N stretch modes appear at 2302 and 2306 cm⁻¹ for two and four defective SBU clusters, respectively. These peaks may correspond to the doublet peaks of experimental ν (CN)_{LA} (2301 and 2311 cm⁻¹). It is also possible that the $\nu(CN)_{LA}$ mode for cluster (b) at 2303 cm⁻¹ corresponds to the experimental 2301 cm⁻¹ mode, although the less favorable binding energy for cluster (b) might indicate a lower concentration of such sites.

We analyzed the $\nu(OH)$ vibrational frequencies of the hydroxylated SBU in clusters (a), (c), and (d) of Figure 7. The $\nu(OH)$ peak appears as a monomodal band shape at 3678 cm⁻¹ prior to the adsorption of CH₃CN in Figures S18 and 4a, which indicates all μ_2 -OH have the same environment. Cluster (a) has four symmetric μ_3 -OH groups and generates a monomodal $\nu(OH)$ band. Cluster (c) has one μ_1 -OH and two different μ_3 -OH environments, which generates trimodal ν (OH) lineshapes and cluster (d) has only one μ_1 -OH group peak. The computational $\nu(OH)$ peaks for clusters (a), (c), and (d) prior to and after adsorption are shown in Figure S32. After CD₃CN adsorption, the ν (OH) band of cluster (a) is 2 cm^{-1} blue-shifted and that of cluster (d) is 45 cm⁻¹ red-shifted and the three peaks of cluster (c) are either blue or redshifted for μ_3 -OH and μ_1 -OH groups, respectively. The ν (OH) peaks of cluster (a) are well matched to the experimental observations before and after adsorption of CH₃CN, but the peaks of clusters (c) and (d) are not observed in the experiment. Thus, we believe that defects corresponding to clusters (c) and (d) are present at very low concentrations in our samples.

CONCLUSIONS

FT-IR and TPD-MS studies of acetonitrile adsorption performed under UHV at 100 K show that most molecules remain on the external surface upon adsorption and that internal sites are not initially probed. This suggests that experiments performed in a typical adsorption–desorption cycle must account for mass transport properties to accurately probe sites within MOFs under cryogenic UHV environments. Thermal activation of UiO-67 MOFs induces the formation of Lewis acid sites of varying strengths, as revealed by blueshifts in the ν (CN) mode of adsorbed CD₃CN. TPD-MS results show that CH₃CN interacts with UiO-67 moieties with a

binding energy of ca. 63 kJ/mol for UiO-67 activated to 473 K. Following CD₃CN diffusion into the UiO-67 crystallite, FT-IR spectroscopy reveals a variety of interactions between CD₃CN and UiO-67. The CD₃CN C–D stretching modes, ν (CD)_s and $\nu(CD)_{ast}$ decrease in intensity upon CD₃CN diffusion into the MOF, while the $\nu(CN)_{HB} + \nu(CN)_{LA}$ modes increase in intensity, showing disproportionate infrared intensity behavior. This cautions the use of integrated infrared absorbance as a metric to determine the concentration of probe molecules inside a MOF. Upon CD₃CN adsorption on UiO-67 thermally activated beyond its dehydroxylation temperature, a blueshifted $\nu(CN)$ doublet, $\nu(CN)_{LA}$ appears at 2301 and 2311 cm⁻¹, suggesting the presence of multiple sites of differing Lewis acidities. We hypothesize that the band at 2311 cm⁻¹ is a result of probing Lewis acid sites present in different nodal structures present in a thermally activated MOF. Based upon the frequencies of the $\nu(CN)_{LA}$ doublet, thermally activated UiO-67 appears to contain stronger Lewis acidic sites compared to those typically found in hydroxylated UiO-67 and its metal oxide counterpart, ZrO₂. Finally, CD₃CN appears to be a versatile active probe for probing OH groups and the relative Lewis acidities of open metal sites. These spectral features reveal the power of CD₃CN as a vibrational probe of defect sites in UiO-67. Our studies not only highlight the importance of analyte diffusion into a material to elucidate catalytic and surface properties but also show that close attention must be paid to discern whether diffused probe molecules obey the Beer-Lambert law.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00639.

UiO-67 sample characterization, MS of CH_3CN and CD_3CN , FT-IR spectra of UiO-67 before and after CD_3CN adsorption, FT-IR spectra of UiO-67 after CO adsorption, rationale for diffusion hold temperatures, background behind Beer–Lambert law discussions, relevant vibrational mode assignments, and additional theoretical structures (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

DFT, density functional theory; FT-IR, Fourier transform infrared; MOF, metal-organic framework; TP-IR, temperature-programmed infrared; TPD-MS, temperature-programmed desorption mass spectrometry; UHV, ultra-high vacuum; UiO, University of Oslo

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