

Molecular CO₂ Storage: State of a Single-Molecule Gas

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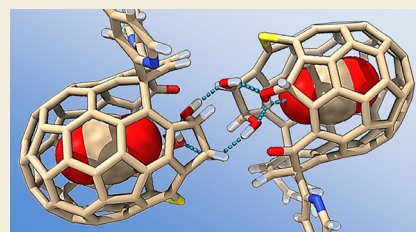
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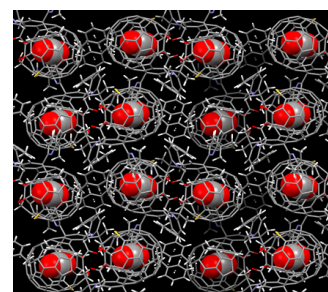
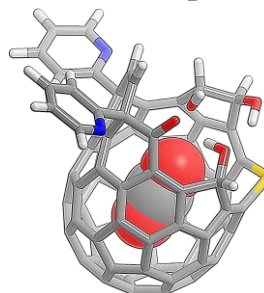
ABSTRACT: CO₂ evolution is one of the urgent global issues; meanwhile, understanding of sorptive/dynamic behavior is crucial to create next-generation encapsulant materials with stable sorbent processes. Herein, we showcase molecular CO₂ storage constructed by a [60]fullerenol nanopocket. The CO₂ density reaches 2.401 g/cm³ within the nanopore, showing strong intramolecular interactions, which induce nanoconfinement effects such as forbidden translation, restricted rotation, and perturbed vibration of CO₂. We also disclosed an equation of state for a molecular CO₂ gas, revealing a very low pressure of 3.14 rPa (1 rPa = 10^{−27} Pa) generated by the rotation/vibration at 300 K. Curiously enough, the CO₂ capture enabled to modulate an external property of the encapsulant material itself, i.e., association of the [60]fullerenol via intercage hydrogen-bonding.

KEYWORDS: carbon dioxide, nanocarbon, single molecule, supramolecular assembly, open-[60]fullerene



Solid sorbent systems for CO₂ capture/storage have been recognized as viable generators of a recyclable carbon source to tackle the global issue that plenty of CO₂ has been continuously emitted and accumulated in the course of industrial and biological processes.¹ As solid sorbents, porous materials such as zeolite,² mesoporous silica,³ and metal–organic frameworks (MOFs)⁴ have been developed in materials science, targeting efficient/selective capture and facile release of CO₂ with a low energy cost. Within the sorbents, CO₂ is captured by chemisorption and/or physisorption where CO₂ is converted into carbamate species by a surface-functionalized interior for the former, while, in the latter case, it binds to Lewis acidic/basic sites such as metal centers and/or active ligands via weak intermolecular interactions.⁵

High polarizability and quadrupolar characteristics of CO₂, however, cause a labyrinth of a physical picture on sorptive/dynamic behavior through a mixed interplay of dispersion forces and electrostatic interactions.⁶ In addition, at higher CO₂ coverages, it undergoes dimerization and/or a change in coordinates from linear to bent within pores.⁷ These multiple factors interfere with each other, thus severely reducing opportunities to gain definitive mechanistic insights into chemisorption/physisorption as well as the physical nature of the confined CO₂ gas, both of which have been poorly understood on a molecular scale.⁸ Hence, molecular CO₂ storage that could experimentally model simple interior sorption is highly demanded for further designing pore functionalities of encapsulant materials. Herein, we focus on open-[60]fullerenols⁹ (Figure 1), which are suitable for exploiting the nanoconfinement effect of captured species such as the acid/base character of gaseous H₂O¹⁰ and paramagnetism of NO.¹¹ In this paper, we examined the sorptive/dynamic behavior and equation of state for a single

A molecular CO₂ storage

- ✓ Fluid dynamics of a single-molecule CO₂ gas
- ✓ Rotational/vibrational dynamics of nanoconfined CO₂
- ✓ Property control of a [60]fullerene container by internal CO₂

Figure 1. [60]fullerene-based molecular CO₂ storage.

molecule of CO₂ gas as well as the nanoconfinement effect on its vibrational behavior. We also discuss a remote property modulation of the [60]fullerene container, which is caused by the internal CO₂ molecule.

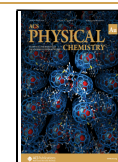
Precursor host **1** contains water, nitrogen, and argon owing to a spontaneous encapsulation.¹² To gain a reasonable occupancy of CO₂ by emitting the precaptured species, CO₂ insertion was performed in *o*-dichlorobenzene (ODCB) at 130 °C under 9000 atm (Figure 2a), while CO₂ could pass through

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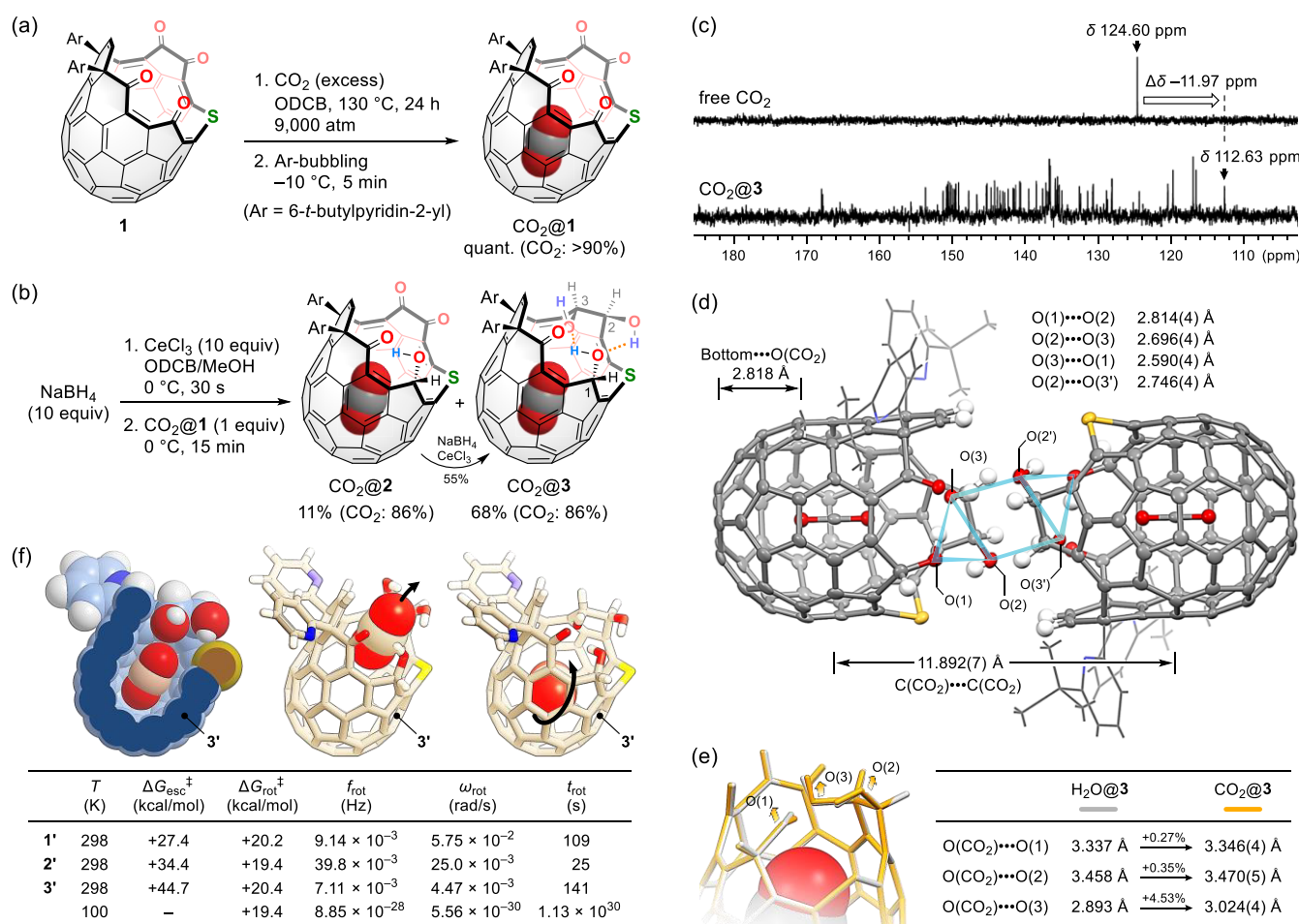


Figure 2. (a) Placing gaseous CO₂ inside **1**. (b) Synthesis of molecular CO₂ storage. (c) ¹³C NMR spectra (500 MHz, CDCl₃/CS₂ (1:1)) of free CO₂ and CO₂@**3**. (d) Crystal structure of (CO₂@**3**)₂ showing thermal ellipsoids at 50% probability (solvent molecules are omitted for clarity). (e) Overlay of crystal structures for H₂O@**3** and CO₂@**3** with selected bond lengths. (f) Thermodynamic parameters for CO₂ inside **1'**, **2'**, and **3'** (Ar = 2-pyridyl; B3LYP-D3/6-31G(d); Δ*G*[‡], barriers for escape/rotation; *f*_{rot}, rotational frequency; ω_{rot}, angular velocity; *t*_{rot}, time required for a full turn of 2π radians).

the orifice even under ambient conditions. The occupancy was determined to be >90% from a signal splitting of the addends by ¹H NMR. After removing CO₂ dissolved in ODCB by Ar bubbling at −10 °C, the Luche reduction was applied to afford CO₂@**2**¹³ and CO₂@**3** (Figure 2b). The occupancy for CO₂@**3** was enriched to be 100% from 86% by recycle HPLC. The presence of captured CO₂ was confirmed by ¹³C NMR (500 MHz, CDCl₃/CS₂ (1:1)) showing its signal at δ 112.63 ppm, which was higher-field shielded, by Δδ −11.97 ppm, from free CO₂ (δ 124.60 ppm), owing to the [60]fullerene aromaticity¹⁴ (Figure 2c). The X-ray diffraction (XRD) analysis at 100 K revealed a dimeric configuration of CO₂@**3** structured by multiple hydrogen bondings arranged in a chair-like shape (Figure 2d), being reminiscent of fullertubes.¹⁵ Within the crystal, the two CO₂ molecules are precisely separated with a distance of 11.892(7) Å on a shared axis. Captured CO₂ most likely interacts with the [60]fullerenol upon seeing close contacts with the carbon wall. The amount of adsorbed CO₂ in crystal (Figure 1) was estimated to be 0.247 cm³/cm³ (1 atm, 25 °C), which is smaller than those for MOFs (90–200 cm³/cm³).¹⁶ However, the CO₂ density in nanopore (*ρ*) is as large as 2.401 g/cm³, which exceeds the highest value reported among MOFs (0.955 g/cm³)¹⁶ and is 2-fold larger than that of liquid CO₂ (1.178 g/cm³ at the triple point¹⁷), indicating a

dense packing of molecular CO₂ within the nanocavity. The crowded arrangement of the three hydroxy groups renders a pore volume (*V* = 30.4 Å³) smaller by −8.9% than **1** (33.4 Å³),¹² which contributes to the dense confinement. Figure 2e illustrates a structural overlay of H₂O@**3**¹⁰ and CO₂@**3** obtained by XRD, unveiling the steric repulsion, which results in an extrusion of the three hydroxy groups toward the outside, by up to +4.53%, with a central focus on the oxygen atom in CO₂.

Since a release barrier of CO₂ from **3'** (Ar = 2-pyridyl) was computed to be Δ*G*[‡] + 44.7 kcal/mol at 298 K, **3** could be regarded as permanent CO₂ storage, while CO₂ escape is probable for **1'** (Figure 2f). Within the nanopore, CO₂ rotates with an activation barrier of Δ*G*[‡] + 20.2 kcal/mol, suggestive of a very slow rotation with rotational frequency *f*_{rot} (7.11 mHz) and time *t*_{rot} (141 s). At 100 K, a full turn requires 1.13 × 10^{−30} s so that the rotation of CO₂ is forbidden under the XRD conditions.

Release rates *k* of CO₂@**1** were measured in CDCl₃ by ¹H NMR (Figure 3a), affording thermodynamic parameters: Δ*G*[‡] + 25.1 ± 1.0 kcal/mol, Δ*H*[‡] 22.5 ± 0.7 kcal/mol, and Δ*S*[‡] −8.96 ± 2.24 cal/(K·mol). Upon assuming the release event being ideal fluid dynamics on an atmospheric relief of a

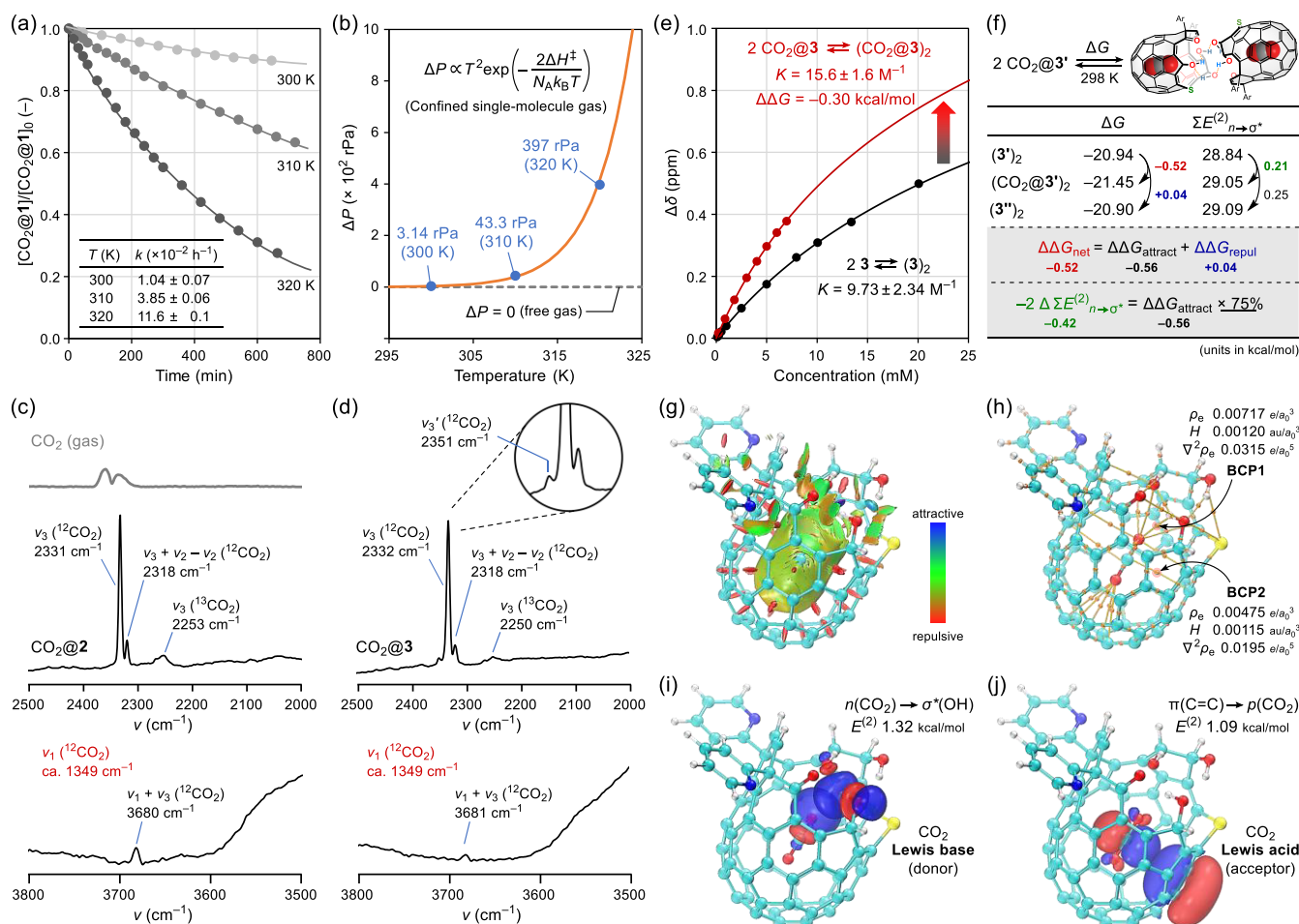


Figure 3. (a) Release rates of CO₂ from **1** in CDCl₃. (b) P–T curve of a single molecule of CO₂ gas in **1**. (c,d) IR spectra of free CO₂, CO₂@**2**, and CO₂@**3** (300 K). (e) Binding constants *K* with stabilization energy ΔΔ*G* induced by CO₂ in **3**, determined by ¹H NMR (500 MHz, CDCl₃, 300 K). (f) Calculated stabilization energies Δ*G* upon dimerization with interaction energies Σ *E*⁽²⁾ of intermolecular hydrogen-bonding (B3LYP-D3/6-31G(d,p)). 3'' is a distorted empty cage whose coordinates originate from CO₂@3'. (g) NCI map of CO₂@3'. (h) BCPs and BPs with selected density values. (i,j) NBOs and interaction energies for CO₂@3'. All calculations were conducted at B3LYP-D3/6-31G(d,p).

nanoscale vessel containing a CO₂ gas, we applied Bernoulli's equation to describe the conservation of momenta:

$$P_1 = P_2 + \frac{\rho v_2^2}{2}$$

where *P* is static pressure and *v* is velocity. Note that the second term, i.e., dynamic pressure, is zero at the initial state due to *v*₁ = 0. The density of CO₂ is defined by ρ = *M*/(*N_AV*) where *M* is molecular weight of CO₂ and *N_A* is Avogadro's constant. The time required for releasing a half quantity of a molecular CO₂ gas (equal to 0.5*V*) is then expressed by

$$t_{1/2} = \frac{0.5V}{Av_2} = \frac{V}{2A} \sqrt{\frac{M}{2N_A V(P_1 - P_2)}}$$

where *A* is the orifice area (4.09 Å²). Given that the physical event obeys a first-order reaction characterized by *t*_{1/2}, which is measurable by a kinetic study on an ensemble of CO₂@**1** (Figure 3a), the transition state theory gives *t*_{1/2} as a function of temperature *T*:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{h \ln 2}{k_B T} \exp\left(\frac{\Delta H^\ddagger - T \Delta S^\ddagger}{N_A k_B T}\right)$$

where *h* and *k_B* are Planck and Boltzmann constants, respectively. Since the dynamic pressure at the final state corresponds to the loss of pressure (Δ*P* = *P*₁ - *P*₂), Δ*P* is consequently associated with a function of *T*:

$$\Delta P = CT^2 \exp\left(-\frac{2\Delta H^\ddagger}{N_A k_B T}\right)$$

$$C = \frac{MV}{8N_A} \cdot \left(\frac{k_B}{Ah \ln 2}\right)^2 \exp\left(\frac{2\Delta S^\ddagger}{N_A k_B}\right)$$

This is regarded as an equation of state for a single-molecule gas captured within the nanocavity. Figure 3b shows a P–*T* curve of a single molecule of CO₂ gas. The dynamic pressure at 300 K was estimated to be Δ*P* = 3.14 rPa (1 rPa = 10⁻²⁷ Pa), which is far smaller than *P*₁ = 102 hPa. Even at 1000 K, it reaches only 3.00 mPa. This is because of a molecular vibration/rotation as a major contributor to the dynamic pressure, while the translational motion is exhaustively forbidden within the cavity. According to the equation, even under d*T* = d*V* = 0, the gaseous molecule attains an eigen pressure loss. This is in stark contrast to an ensemble whose equation of state (*PV* = *k_BT*, Δ*P* = 0 under constant *T* and *V*)

is derived from kinetic theory of gases, solely depending upon translational motion.

To further study rotational/vibrational dynamics of the confined CO₂ gas, we measured IR spectra at 300 K (Figure 3c,d). Linear triatomic CO₂ with a $D_{\infty h}$ symmetry has four fundamental modes of vibration including symmetric and antisymmetric stretching (ν_1 and ν_3) as well as doubly degenerated bending (ν_2), where only ν_2 and ν_3 are IR active. Whereas a band overlap in a fingerprint region was unable to discriminate ν_2 from others originating from skeletal vibration of the carbon cage, ν_3 (¹²CO₂) was found at 2331 cm⁻¹ for CO₂@2 and 2332 cm⁻¹ for CO₂@3 as a sharp band, which differs from atmospheric CO₂ showing a broad band (2349 cm⁻¹)⁶ caused by a vibration/rotation coupling (Figure 3c). Within the nanocavity, however, the rotational frequency of CO₂ (10^{-3} – 10^{-2} Hz, Figure 2f) is rather larger than the time scale of molecular vibration (10 fs–1 ps),¹⁸ which significantly relaxes the coupling. The observed red-shift of $\Delta\nu_3$ –17 to –18 cm⁻¹ relative to free CO₂ is comparable to those observed for CO₂ in typical MOFs (ν_3 2335 cm⁻¹),^{7b} implying the presence of interactions to a similar extent. The two bands at lower wavenumbers correspond to a hot band ($\nu_3 + \nu_2 - \nu_2$) and satellite (ν_3 (¹³CO₂)).¹⁹ At a higher wavenumber, CO₂@3 showed a small band (ν_3' 2351 cm⁻¹), which is unlikely to be found for CO₂@2. A metastable orientation of the three hydroxy groups in CO₂@3 would be a possible explanation, as supported by computational studies (Figure S12). Importantly, a combination band ($\nu_1 + \nu_3$) was observed at 3680 cm⁻¹ for CO₂@2 and 3681 cm⁻¹ for CO₂@3. From the combination tone, ν_1 was estimated to be ca. 1349 cm⁻¹, which is red-shifted by $\Delta\nu_1$ ca. –39 cm⁻¹ relative to free CO₂ (ν_1 1388 cm⁻¹).⁶ Though Fermi resonance might not be neglected, this value is as large as 2-fold $\Delta\nu_3$, being suggestive of a strong nanoconfinement effect on the symmetric stretching (ν_1), which offers a larger vibrational displacement than that of the antisymmetric one (ν_3).

To our surprise, the captured CO₂ gas enabled to modulate an external property of the encapsulant material itself. The association constant of CO₂@3 in CDCl₃ at 300 K was measured to be $K = 15.6 \pm 1.6$ M⁻¹, which is 1.6-fold larger than that of empty 3 (9.73 ± 2.34 M⁻¹) (Figure 3e). This is suggestive of the preferred association for the latter by $\Delta\Delta G$ –0.30 kcal/mol, being in good accordance with the calculated value of $\Delta\Delta G_{\text{net}}$ –0.52 kcal/mol (Figure 3f), which includes attractive (–0.56 kcal/mol) and repulsive (+0.04 kcal/mol) interactions mainly caused by better hydrogen-bonding ($-2\Delta\Sigma E^{(2)}$ –0.42 kcal/mol) and geometrical distortion upon CO₂ capture (Figure 2e), respectively.

A reduced density gradient (RDG) isosurface²⁰ was plotted for CO₂@3' (Figure 3g), showing weak noncovalent interactions (NCI), around the CO₂ molecule, which were characterized by multiple bond critical points (BCPs) and bond paths (BPs) (Figure 3h).²¹ A positive Laplacian of electron density $\nabla^2\rho_e$ and total electron energy density H at BCP1 and BCP2 imply pure closed-shell interactions without a covalent nature. Natural bond orbital (NBO) analysis showed interaction energies as large as $E^{(2)}$ 1.32 ($n(\text{CO}_2) \rightarrow \sigma^*(\text{OH})$) and 1.09 ($\pi(\text{C}=\text{C}) \rightarrow p(\text{CO}_2)$) kcal/mol, respectively (Figure 3i,j). These results are decisive of the confined CO₂ molecule potentially acting as both a Lewis base and Lewis acid.

In conclusion, we designed molecular CO₂ storage as the simplest experimental model for revealing clear physical pictures on the chemical/dynamic processes of a molecular

CO₂ gas confined within a nanoscale cavity, which are otherwise uncertain in known sorbent systems due to competing complex interactions. The combined analyses of XRD, IR, and computations demonstrated the presence of intramolecular interactions in CO₂@3, which cause nanoconfinement effects on translational, vibrational, and rotational motions of captured CO₂, where it acts as both a Lewis base and Lewis acid. The release event for CO₂@1 revealed the equation of state for a single-molecule gas at imperceptible pressure levels. The captured CO₂ gas modulated an external property of the encapsulant material itself owing to the better arrangement of intermolecular hydrogen-bonding. These findings would facilitate further understandings of chemical/physical events of CO₂ accommodated within a variety of sorbent materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsphyschemau.3c00068>.

Detailed experimental procedures, characterization data, and computational results (PDF)

Crystallographic data (CIF)

Accession Codes

CCDC 2301301 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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