Supporting Information

Mathematical modeling of gas desorption from a metal organic super container cavity filled with stored N_2 gas at critical limits

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Supplemental Discussion:

For the system considered, where intermolecular interactions are the most important, the MM+ FF is sufficient. The MM2 force field may provide correction in regimes of low pressure and low kinetic energy, where hydrogen bonding plays important role. The correlation between the desorption rate, retention rate, and the adsorption rate are left for future investigation. Application of this model to different gases would require two steps: (a) change of the model parameter describing the size of the gas molecule and (b) re-calibration of the fitting parameter F_c based on explicit molecular dynamics data for each specific gas. A preliminary step of applying the approach of this paper to H2 is reported in **Figure 5**. However, an extensive analysis, calibration, and benchmarking have to be done for providing confident conclusions/trends, which goes beyond the format of this paper.

Equations for sequence of gas molecule escape events

At $t = 0$, all I^{th} nitrogen gas atoms are removed from the center of mass to the distance smaller than the cavity radius, $|\vec{R}_I(t = 0) - \vec{R}_{cm}| < R_0$. At the initial time, the nitrogen atoms can be ordered according to their distance from center of mass, shown in Eqn. S1

$$|\vec{R}_1(t = 0) - \vec{R}_{cm}| < |\vec{R}_2(t = 0) - \vec{R}_{cm}| < \ldots < |\vec{R}_{N-1}(t = 0) - \vec{R}_{cm}| < |\vec{R}_N(t = 0) - \vec{R}_{cm}| < R_0 \qquad \text{(S1)}$$

As time passes, some of the nitrogen atoms and molecules move away from the center of mass. At a specific time t' one of the atoms starts to penetrate through the cavity wall, as described in Eqn. S2.

$$|\vec{R}_1(t') - \vec{R}_{cm}| < |\vec{R}_2(t') - \vec{R}_{cm}| < \ldots < |\vec{R}_{N-1}(t') - \vec{R}_{cm}| < |\vec{R}_N(t') - \vec{R}_{cm}| = R_0 \qquad \text{(S2)}$$

At later time $t > t'$, one of the atoms leaves the cavity, in Eqn. S3.

$$|\vec{R}_1(t > t') - \vec{R}_{cm}| < |\vec{R}_2(t > t') - \vec{R}_{cm}| < \ldots < |\vec{R}_{N-1}(t > t^{'}) - \vec{R}_{cm}| < R_0 < |\vec{R}_N(t > t') - \vec{R}_{cm}| \qquad \text{(S3)}$$

Later, at time t” the conjugated nitrogen atom belonging to the same N_2 diatomic molecule crosses the border, as presented in Eqn. S4,

$$|\vec{R}_1(t'') - \vec{R}_{cm}| < |\vec{R}_2(t'') - \vec{R}_{cm}| < \ldots < R_0 = |\vec{R}_{N-1}(t^{''}) - \vec{R}_{cm}| < |\vec{R}_N(t'') - \vec{R}_{cm}| \qquad \text{(S4)}$$

and then departs further away from the cavity wall in a fashion described by Eqn. S5.

$$|\vec{R}_1(t > t'') - \vec{R}_{cm}| < |\vec{R}_2(t > t'') - \vec{R}_{cm}| < \ldots < R_0 < |\vec{R}_{N-1}(t > t^{''}) - \vec{R}_{cm}| < |\vec{R}_N(t > t'') - \vec{R}_{cm}| \qquad \text{(S5)}$$

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$$|\vec{R}_1(t > t'') - \vec{R}_{cm}| < |\vec{R}_2(t > t'') - \vec{R}_{cm}| < \ldots < R_0 < |\vec{R}_{N-1}(t > t^{''}) - \vec{R}_{cm}| < |\vec{R}_N(t > t'') - \vec{R}_{cm}| \qquad \text{(S5)}$$

Estimate of the storage capacity of a MOSC based on liquid nitrogen density.

- $$Cavity\ Volume = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{1.25\ nm \times 10^{-7}\ cm}{2}\right)^3 = 1.023 \times 10^{-21}\ cm^3$$

  $$Density = \frac{32\ molecules}{} \times \frac{28\ amu}{molecule} \times \frac{1.66 \times 10^{-27} kg}{amu} \times \frac{10^3\ g}{kg} \times \frac{}{1.023 \times 1}$$

- $$\frac{g}{mL}\ \rightarrow about\ 1.8\ times\ higher\ than\ liquid\ nitrogen\ \left(\frac{0.81 g}{mL}\right).$$

If you take $1.45\frac{g}{mL}$ and divide by 32, then the density of one nitrogen molecule filling the space would be $0.045\frac{g}{mL}$. Then 0.81 divided by 0.045 = **~18 nitrogen molecules** to achieve a density representative of liquid nitrogen's density.

Table S1. Comparison of the fitting methods for D'_w and D'_C. Linear equation provides best correlation R^2. A quadratic equation gives reasonable fit only for negligible coefficient in front of quadratic term, making it equivalent to linear equation.

	Fitting method	**R^2**
D'_w	$y = 8E\text{-}05x + 0.27$	1.00
	$y = -1E\text{-}20x^2 + 8E\text{-}05x + 0.27$	1.00
	$y = 0.1619x^{0.1073}$	0.9991
	$y = 0.2722e^{0.0003x}$	0.9357
D'_C	$y = 0.0001x + 1.222$	1.00
	$y = 1.2237e^{0.0001x}$	0.9998
	$y = 0.984x^{0.0451}$	0.9273

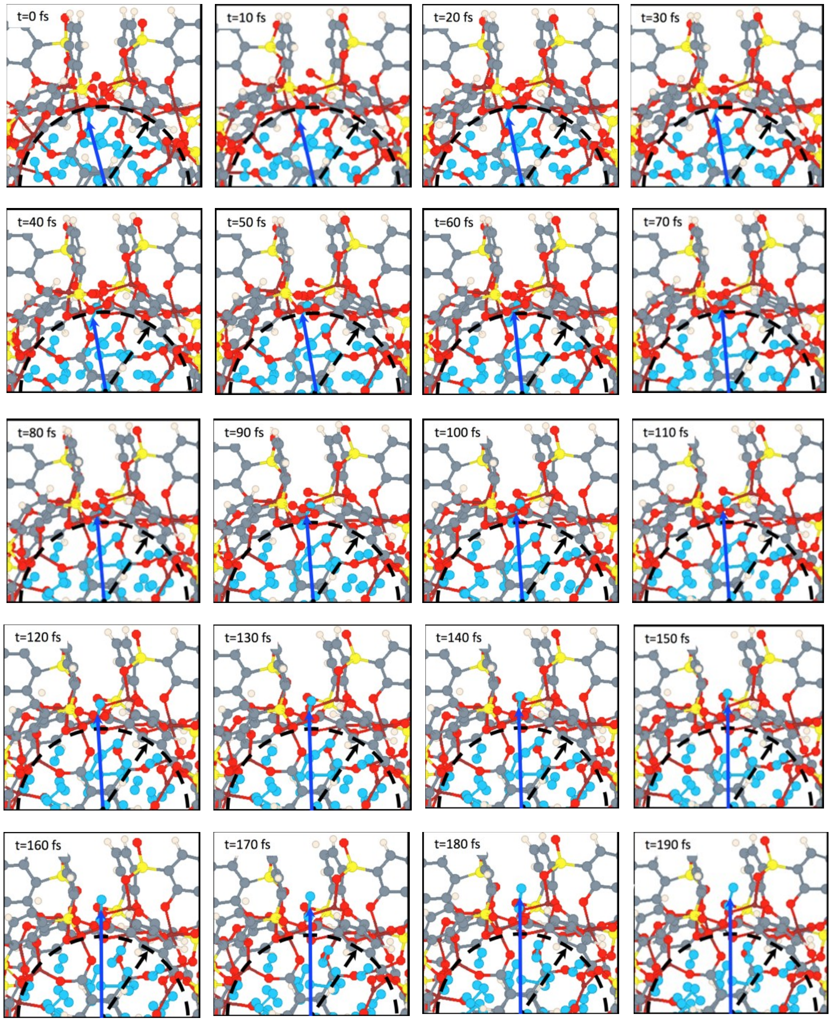

Figure S1. Details on the specific trajectory of molecular dynamics at 250K. Snapshots of MD illustrates the mechanism of thermally activated release of the stored nitrogen molecules from the inner cavity of the MOSC molecule. A cavity of MOSC container molecule is filled with 32 N_2 molecules at a certain density and ramped to ambient temperature, here T=250K. As time passes by, the gas molecules approach the walls of the container and infiltrate through the container walls. The time of desorption is defined based on a comparison of the distance of the desorbing molecule from the center of mass, represented by the blue arrow and the radius of the cavity, represented by a dashed line. According to eqn. 2b, at a time when the molecule is inside the cavity it is considered stored. At a time when the molecule is outside of the cavity, it is considered desorbed. In this specific simulation, the desorption occurs at about seventy femtoseconds from the start of the simulation.

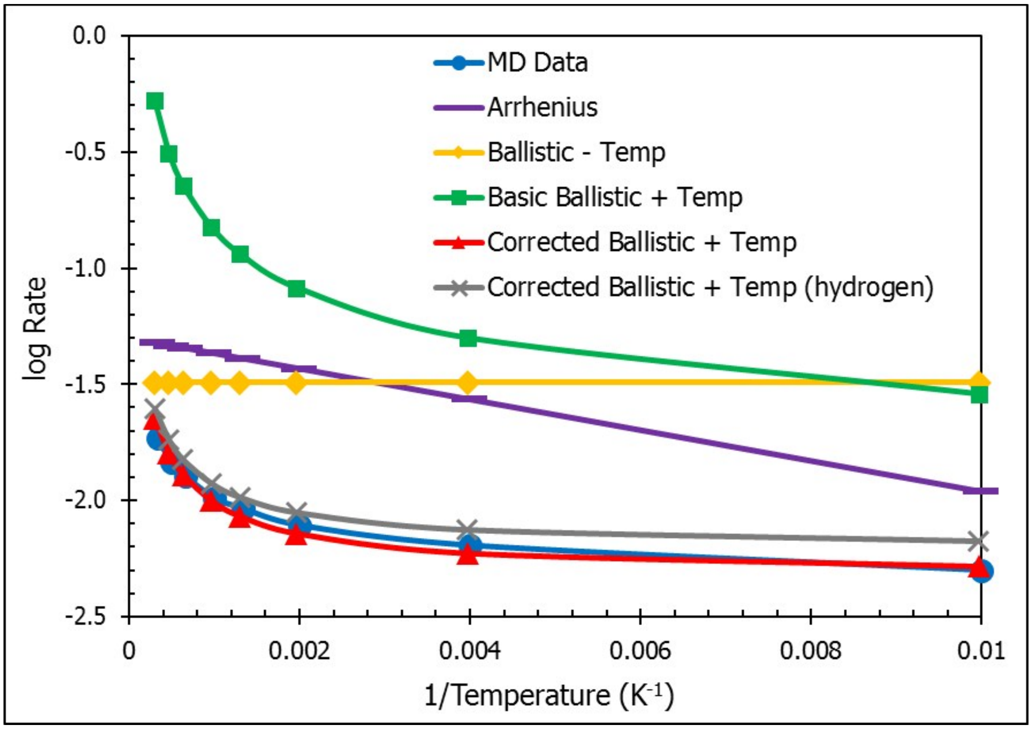

Figure S2. Combined graphs of all mentioned modeling methods. Data from the MD simulation is shown in a blue line with circles, Arrhenius equation in purple with rectangles, ballistic kinetics without temperature dependence in yellow with diamonds, ballistic kinetics with temperature dependence in green with squares, and ballistic kinetics with temperature dependence and correction factors in red with triangles. The purple line with rectangles is the graph obtained by using the activation energy from the MD simulations and plotting the Arrhenius equation (eqn. 4). This purple line does not match the MD data in shape, nor is it in the same region of the graph. However, the Arrhenius line does follow a similar trend found in the MD data, which is that there is a faster desorption rate at higher temperatures. The data based on the derived mathematical equations are also shown. First, the ballistic kinetics equation (eqn. 10) without a temperature dependence in pore size and the average molecule diameter are plotted with a yellow line and diamonds. This derived equation shows the opposite trend expected. Despite this disconnect, once the temperature dependence is added (eqn. 12), a similar shape and trend are seen in the green line with squares. Finally, the equation that was derived for nitrogen gas escape was modified to be used for hydrogen gas escape. It can be seen as the gray line marked with crosses. The overall trend is very similar to the results for nitrogen modeling, but the rate is higher across the range of temperatures.

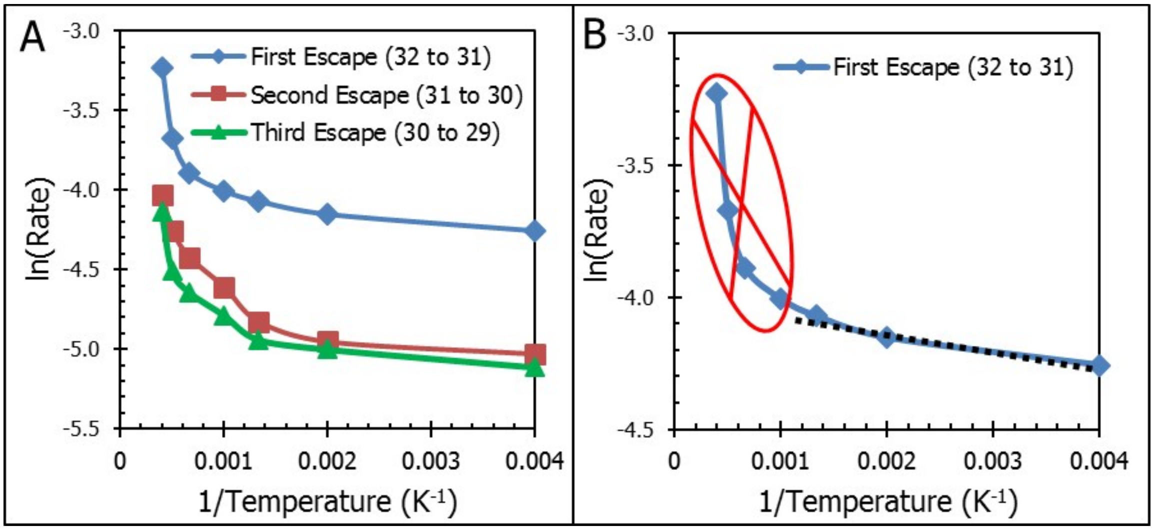

Figure S3 Gas desorption rates, R, are computed for different temperatures and are shown in the Arrhenius format of eqn. 5. Panel **A**: The natural logarithm of gas desorption rates as they depend on the inverse of temperature. Data is shown for multiple escape events of the first three nitrogen molecules. Time is reset between escape events. Panel **B**: The first nitrogen molecule escape data is used to extract the slope of the line. The left-most data points are excluded due to the extremely high temperatures they represent. The slope is used to find the activation energy of the gas escape. Additionally, the $R = R(T)$ dependence deviated from the expected linear behavior of eqn. 5. A specific activation energy can be assigned to each range of temperatures. As one progresses from low to high temperatures (from right to left in an Arrhenius plot), the natural log of $R(T)$ becomes steeper and activation energy becomes lower. The lowering of E_a at high temperatures is explained by a window-opening mechanism.