

Supporting Information

Quantum Sieving Effect of Three-Dimensional Cu-based Organic Framework for H₂ and D₂

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Materials:

The crystal structure of preheated CuBOTf was obtained using a synchrotron X-ray powder diffraction (XRPD) pattern at the Super Photon Ring (SPring-8, Hyogo, Japan). The CuBOTf powder was set in a Lindemann glass capillary (0.30 mm outside diameter), and preheated at 383 K under 1 mPa for 2 h before sealing. The preheating temperature is determined by thermogravimetric analysis (TGA), under a nitrogen flow of 100 mL/min over a range of temperatures from ambient temperature to 1100 K at a heating rate of 5 K/min (fig. S3). The XRPD pattern of the pretreated sample was measured at room temperature with the radiation wavelength of 0.1001 nm. The XRPD pattern was indexed with the indexing program DICVOL91 (S1), after which the structure of CuBOTf was solved by a direct method and refined by the Rietveld technique with the software EXPO2004 (S2).

Adsorption measurement of H₂ and D₂ at low temperature:

H₂ and D₂ adsorption isotherms of CuBOTf at 77 and 40 K were measured with laboratory-designed volumetric adsorption equipment consisting of a gas-handling system and cryostat (Suzuki Shokan) with a He closed-cycle refrigerator (SRDK-205DW, Sumitomo Heavy Industries). Three MKS Baratron gauges (626A) with full-scale ranges of 13.3 Pa, 1.33 kPa, and 133 kPa were attached to the gas-handling system and used for pressure measurements. The temperature of a sample cell mounted on the refrigerator was measured by a silicon diode (DT-470, Lakeshore) and kept constant within ± 0.003 K during the adsorption measurements. All samples for H₂ and D₂ adsorption were outgassed at 383 K for 5 h under 1 mPa before each adsorption measurement. An identical sample and sample cell were used for both H₂ and D₂ adsorption measurements to reduce experimental errors. Thermal transpiration was corrected by using the empirical equation of Takaishi and Sensui (S3).

Determination and calculation of isosteric heat of adsorption:

The isosteric heats of adsorption (q_{st}) for H₂ and D₂ in CuBOTf was obtained from the following equation for adsorption isotherms at 40 K and 77 K:

$$q_{st} = -k_B \left(\frac{\partial \ln P}{\partial (1/T)} \right)_{n_a} \quad (S1)$$

where k_B is the Boltzmann's constant, T and P are the system temperature and pressure, and n_a is the adsorption amount, respectively. The q_{st} for hydrogen isotopes from the fluctuations in the number of adsorbed molecules and total energy during the GCMC simulations was calculated:

$$q_{st} = \frac{5}{2} k_B T - \frac{\langle EN \rangle - \langle E \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (S2)$$

where the total energy E is the sum of kinetic and potential energies of the system. The total energy based on the FH approach is given by (S4),

$$E = \frac{3}{2} N k_B T + \sum_{i < j}^N \beta \left(\frac{dV_{FH,ij}^{ff}}{d\beta} \right) + \sum_i^N \sum_k^{N_s} \beta \left(\frac{dV_{FH,ik}^{sf}}{d\beta} \right) + \sum_{i < j}^N V_{FH,ij}^{ff} + \sum_i^N \sum_k^{N_s} V_{FH,ik}^{sf} \quad (S3)$$

where V_{FH}^{ff} and V_{FH}^{sf} are the pair fluid-fluid and solid-fluid interaction potentials, N is the number of fluid molecules, N_s is the number of the framework atoms in a CuBOTf model, and $\beta = 1/k_B T$. The first term on the right-hand side of eq. (S3) is the kinetic energy of classical molecules, the second and third terms are quantum corrections to the classical kinetic energy, and then the rest are the fluid-fluid and solid-fluid potential energies.

Calculation method of selectivity of D₂ over H₂:

Mixture adsorption isotherms can be predicted from pure-component adsorption isotherms by using ideal adsorption solution theory (IAST) in the absence of the interaction between component gases (S5). This theory is based on the concept of an ideal solution (similar to Raoult's law). Here, assuming the chemical potential in adsorbed phase to be equal to that in gas phase, then,

$$P y_i = P_i^0(\pi) x_i \quad (S4)$$

where P is the total pressure in the bulk phase, $P_i^0(\pi)$ is the pure adsorbate gas pressure for component i that corresponds to the spreading pressure π of the binary mixture, and x_i and y_i are the mole fractions of the component i in the adsorbed and bulk phase, respectively. The spreading pressure can be calculated as

$$\pi(P_i^0) = \frac{RT}{A} \int_0^{P_i^0} n_i(P) d \ln P \quad (S5)$$

where $n_i(P)$ is the adsorption isotherm for the pure component i , and A is the surface area of the adsorbent. In order to calculate $\pi(P_i^0)$, it is convenient if a single-component isotherm can be fitted to

a suitable isotherm function that reduces to Henry's law at low pressures. Therefore, in this study, we used a multiple Langmuir equation as follows.

$$n_i(P) = \sum_{k=1}^3 \frac{c_{ik} b_{ik} P}{1 + b_{ik} P} \quad (\text{S6})$$

The Newton-Raphson method was used to solve the non-linear equations of the spreading pressures of each component, and the molar fraction of component i in the adsorbed phase x_i was obtained. Then, the selectivity of component j over i was calculated as follows:

$$S(j/i) = \frac{x_j/x_i}{y_j/y_i} = \frac{P_i^0}{P_j^0} \quad (\text{S7})$$

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- S2. A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* **32**, 339 (1999).
- S3. T. Takaishi, Y. Sensui, *Trans. Faraday. Soc.* **53**, 2503 (1963).
- S4. H. Tanaka, H. Kanoh, M. Yudasaka, S. Iijima, K. Kaneko, *J. Am. Chem. Soc.* **127**, 7511 (2005).
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Table S1. Potential parameters for the atoms in CuBOTf framework

Parameters without asterisks are taken from the OPLS-AA force field of Jorgensen et al. (5).

Parameters with ^(*) are taken from the OPLS-AA force field of Watkins et al. (6).

Parameters with ^(**) are taken from the UFF (7).

Atom	σ_{ss} [nm]	ϵ_{ss}/k_B [K]
Cu	0.311 [*]	2.517 [*]
O	0.296	105.73
H _{benzene}	0.242	15.10
C _{Benzene}	0.355	35.24
C _{R4C}	0.350	33.23
F	0.295 ^{**}	26.68 ^{**}
S	0.355	125.87
N	0.325	85.59

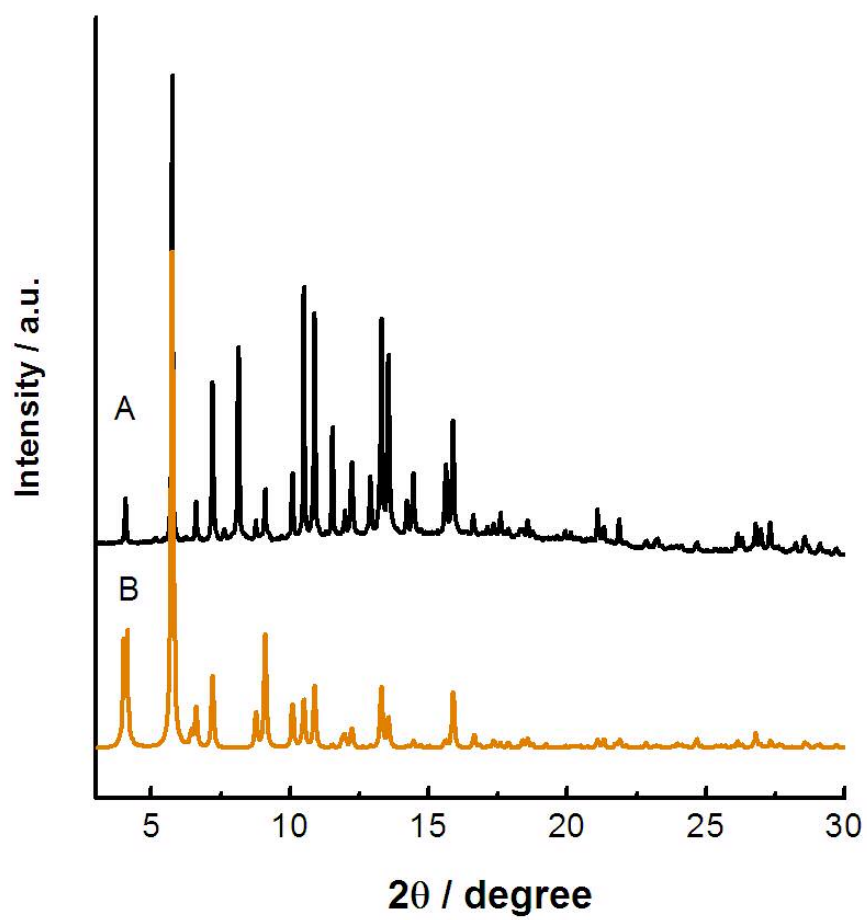


Figure S1. X-ray diffraction patterns of CuBOTf samples and the model structures.

(A) Experimental pattern, (B) pattern calculated from CuBOTf structure.

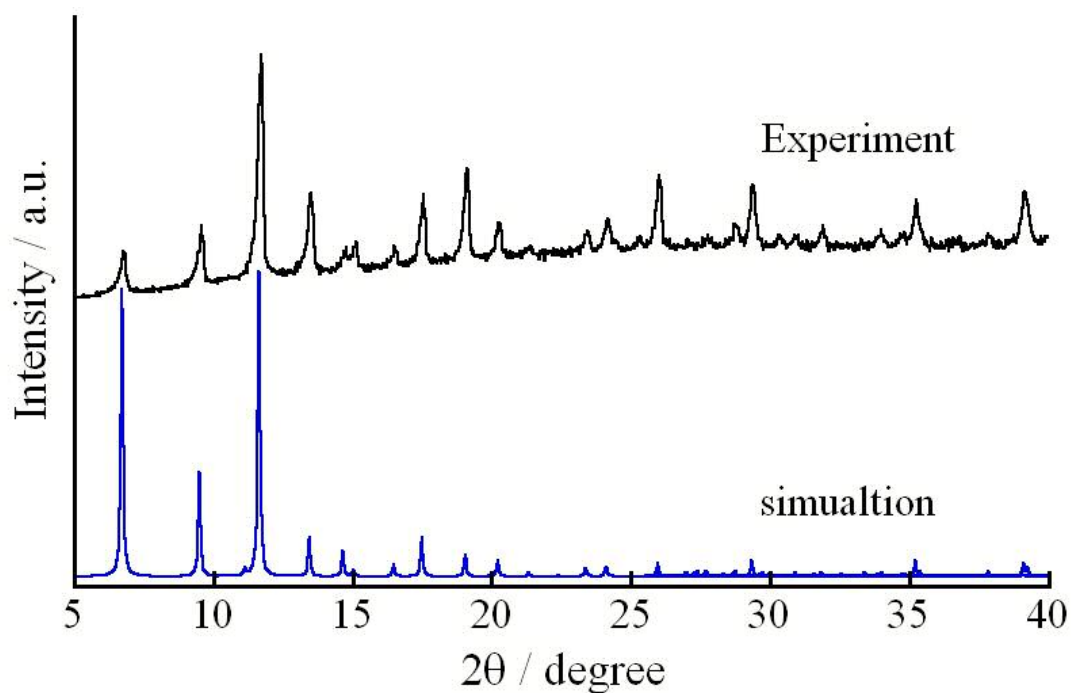


Figure S2. Simulated (black) and experimental (blue) x-ray diffraction patterns of Cu-BTC (Cu K α radiation). The XRD simulation was performed on the crystallographic data reported in the literature¹¹ with the removal of the guest molecules.

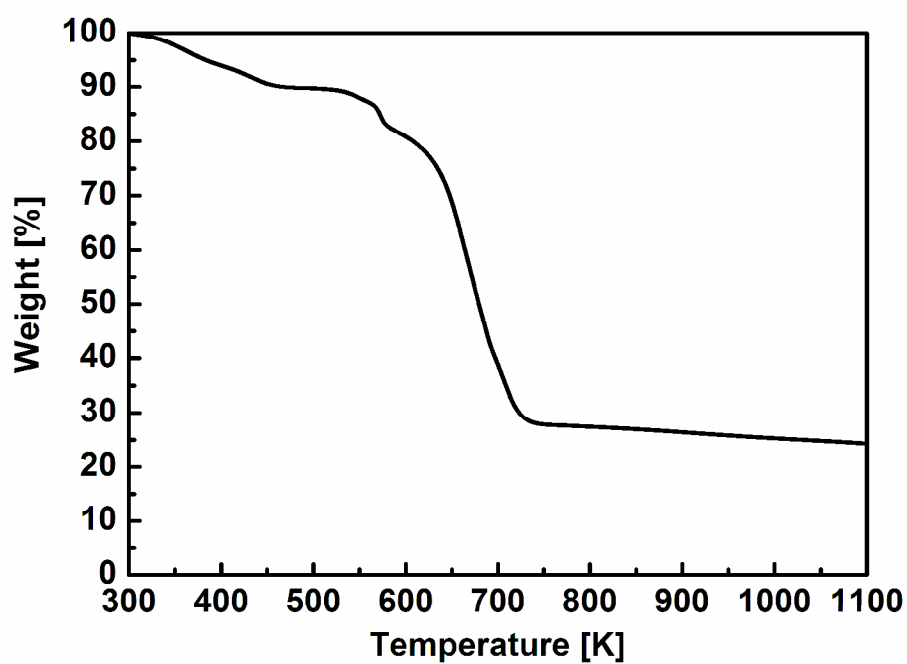


Figure S3. TGA curve of CuBOTf under nitrogen flow

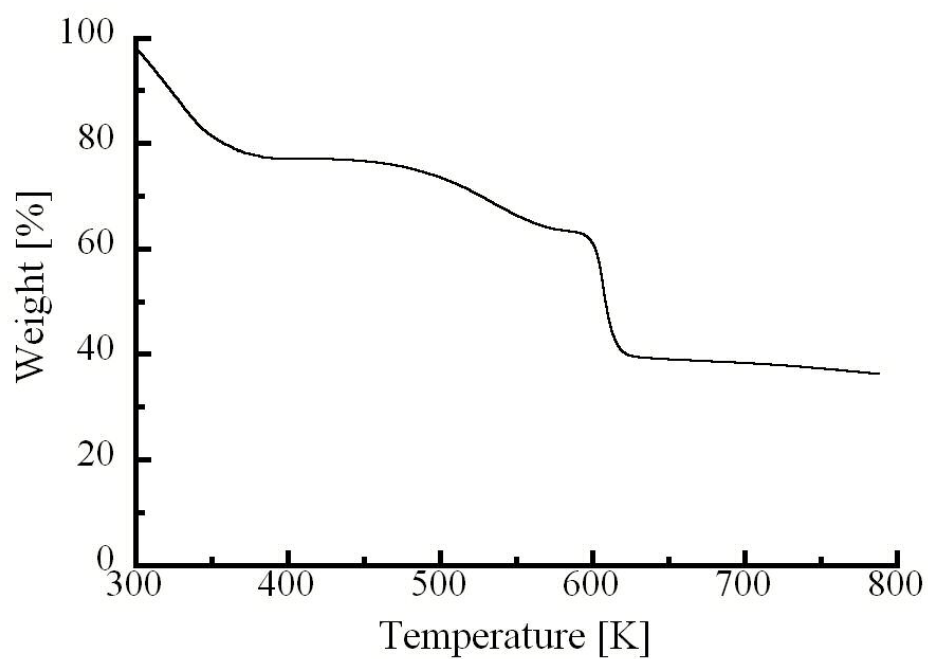


Figure S4. TGA curve of Cu-BTC under nitrogen flow.

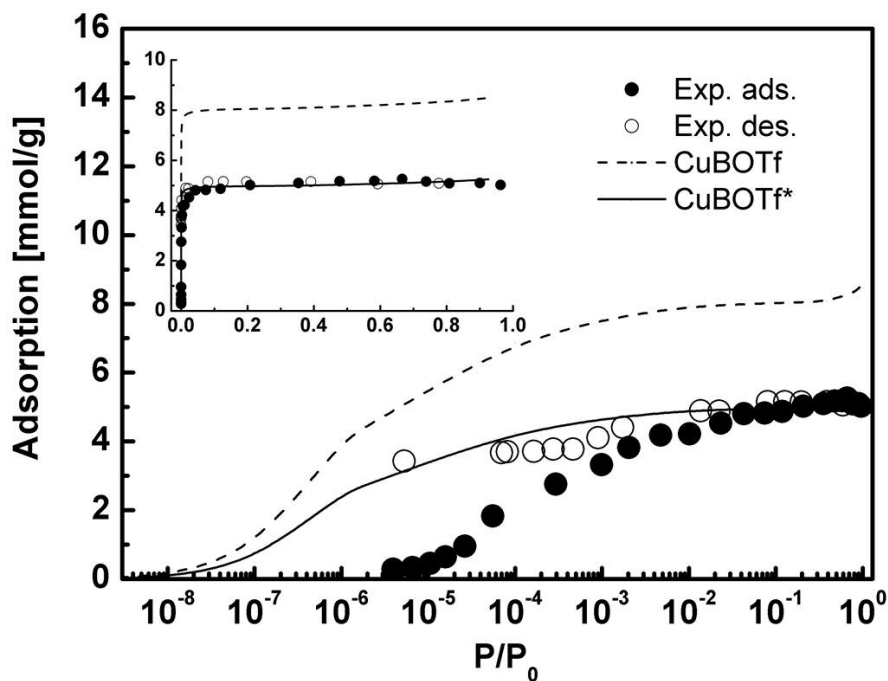


Figure S5. Simulated and experimental N_2 adsorption isotherms of CuBOTf at 77 K. The filled and opened circles represent the experimental adsorption and desorption isotherms, while the lines represent the simulated adsorption isotherms from the respective CuBOTf models. (CuBOTf: simulated isotherm, CuBOTf*: simulated isotherm after a correction with effective nanoporosity factor). The relative pressure is given in logarithmic (Inset is in linear) scales.

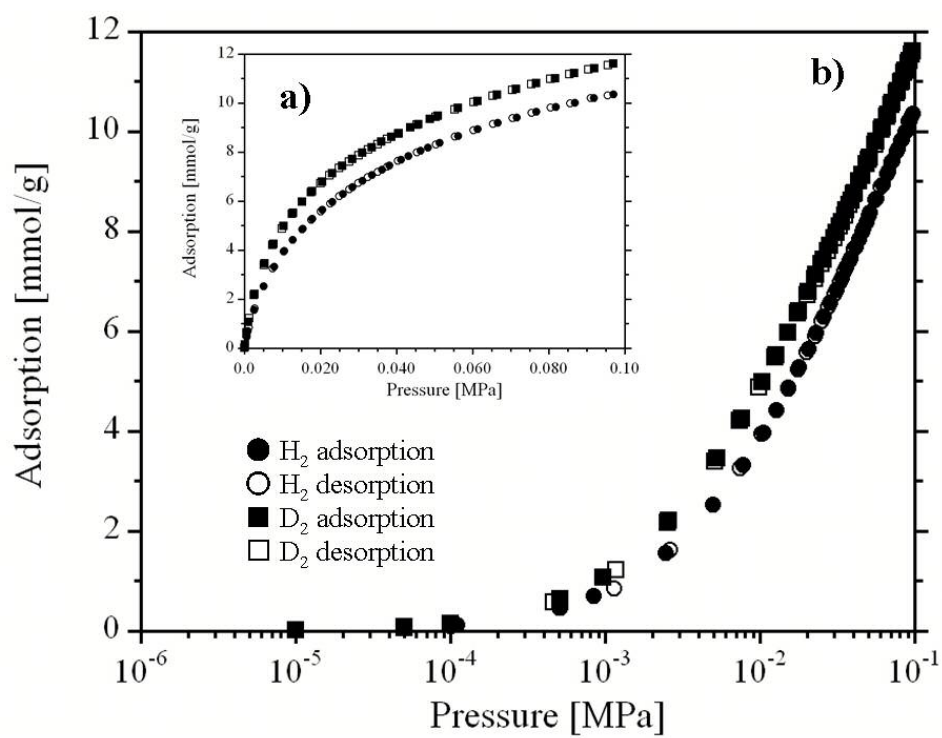


Figure S6. Experimental H₂ and D₂ adsorption isotherms of Cu-BTC at 77 K. The pressures are given in a)linear and b)logarithmic scales.

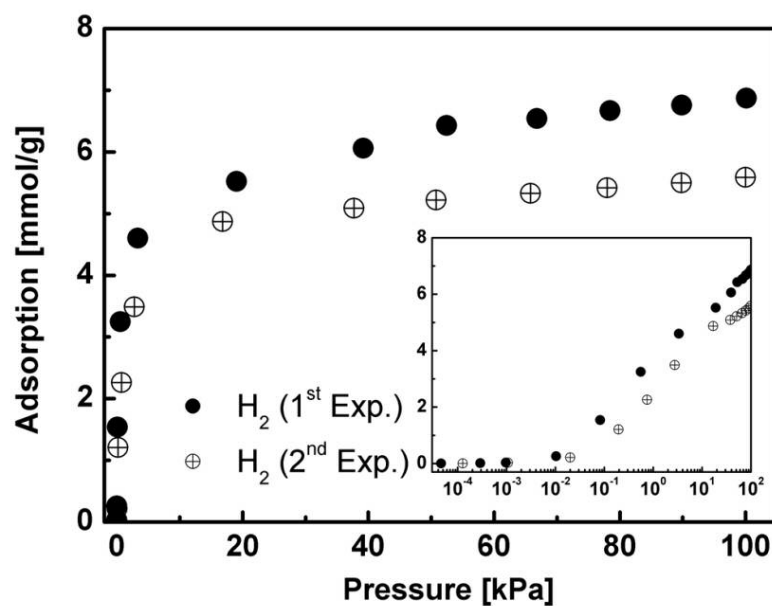


Figure S7. Experimental H₂ adsorption isotherms of CuBOTf at 40 K with different equilibration time: (1st Exp.) Measured at 6 to 12 h, and (2nd Exp.) measured at 3 to 6 h, after introduction of H₂. The pressures are given in linear (Inset is in logarithmic) scales.

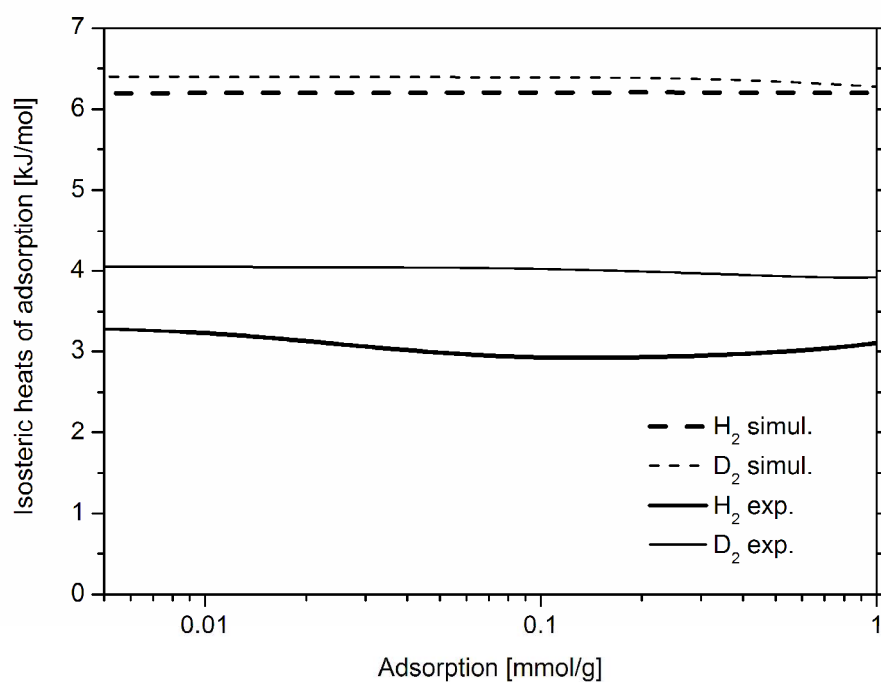


Figure S8. Simulated and experimental isosteric heats of adsorption for H₂ and D₂. Experimental values are shown in solid lines, and simulated values are shown in dashed lines.