Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:

Sizable Dynamics in Small Pores: CO_2 Location and Motion in the α-Mg Formate Metal-Organic Framework

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Table of Contents

Table S1. The extracted wobbling[a] and hopping[b] angles of CO_2 in α-Mg formate, as derived from ^{13}C SSNMR spectra using EXPRESS.[1] Both motional rates are in the fast motion regime (*i.e.*, $\geq 10^7$ Hz) throughout the experimental temperature range.

Temperature (° K)	Wobbling (α, °)	Hopping (β, °)
393	47.5	41
373	47.5	42
353	47.5	44
333	48	45
313	48	45
293	49	42
273	49	39
253	49	36
233	48.5	32
213	48	27
193	47	23
173	45	23

[a] The uncertainty of each wobbling angle is ± 0.1 °. [b] The uncertainty of each hopping angle is 0.2 °.

[1] R. L. Vold and G. L. Hoatson, *J. Magn. Reson.*, 2009, **198**, 57-72.

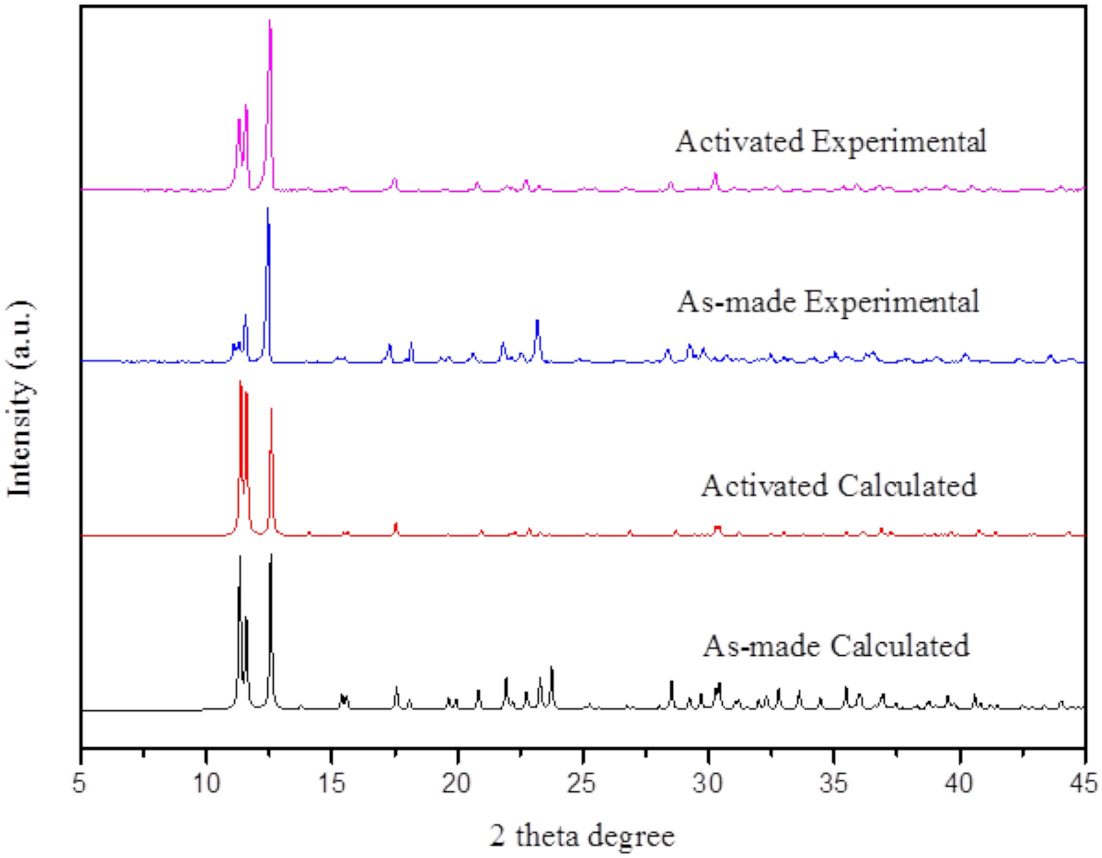

Figure S1. Powder XRD (pXRD) results of the activated and as-made α-Mg formate MOF, along with the calculated pXRD patterns.

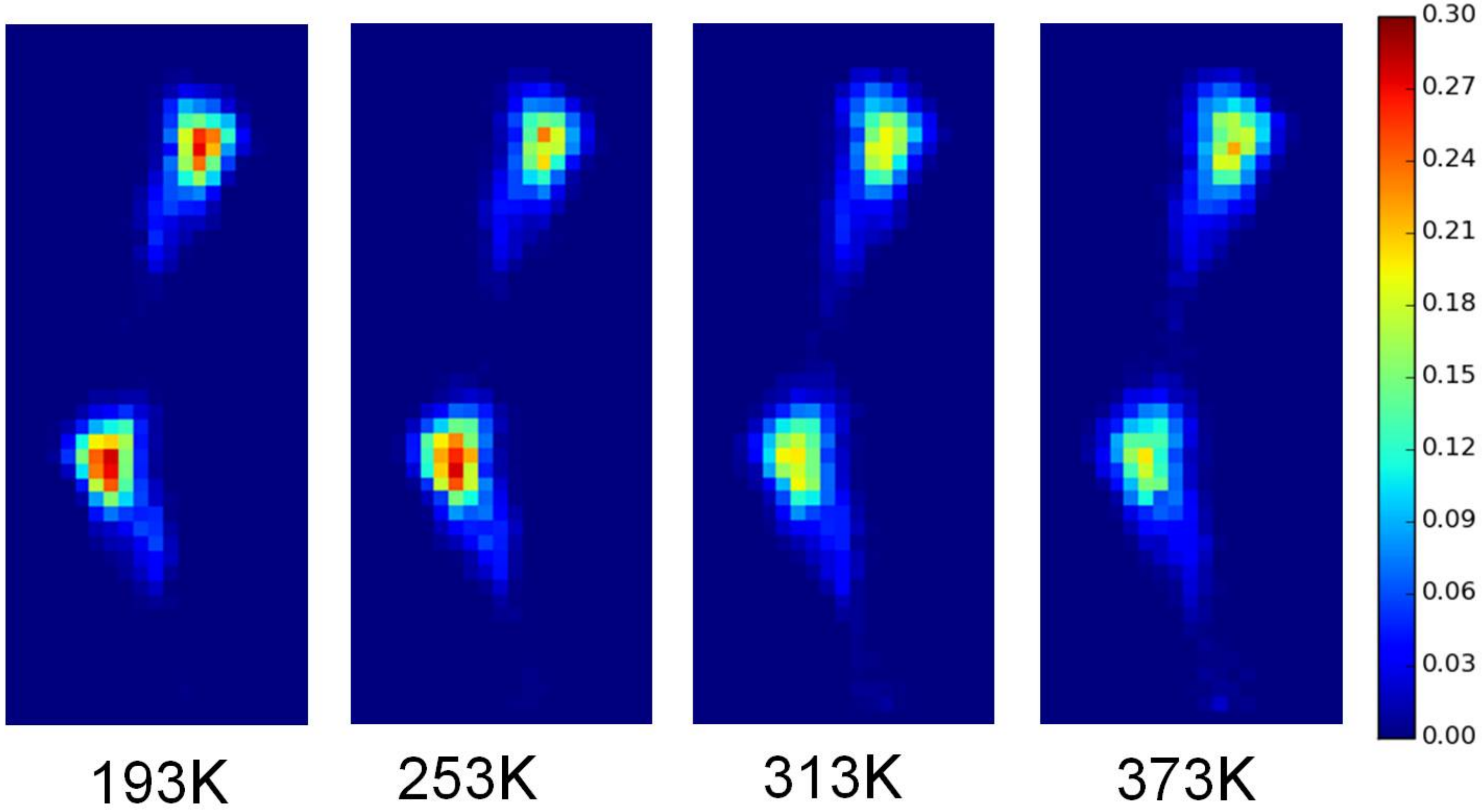

Figure S2. The *xy* plane projection of the distribution of carbon atoms of CO_2 in α-Mg formate at various temperatures, as calculated by MD simulations. The decrease in localized intensity at higher temperatures, and increase in intensity between the maxima, is due to increased CO_2 mobility within the channels of α-Mg formate.

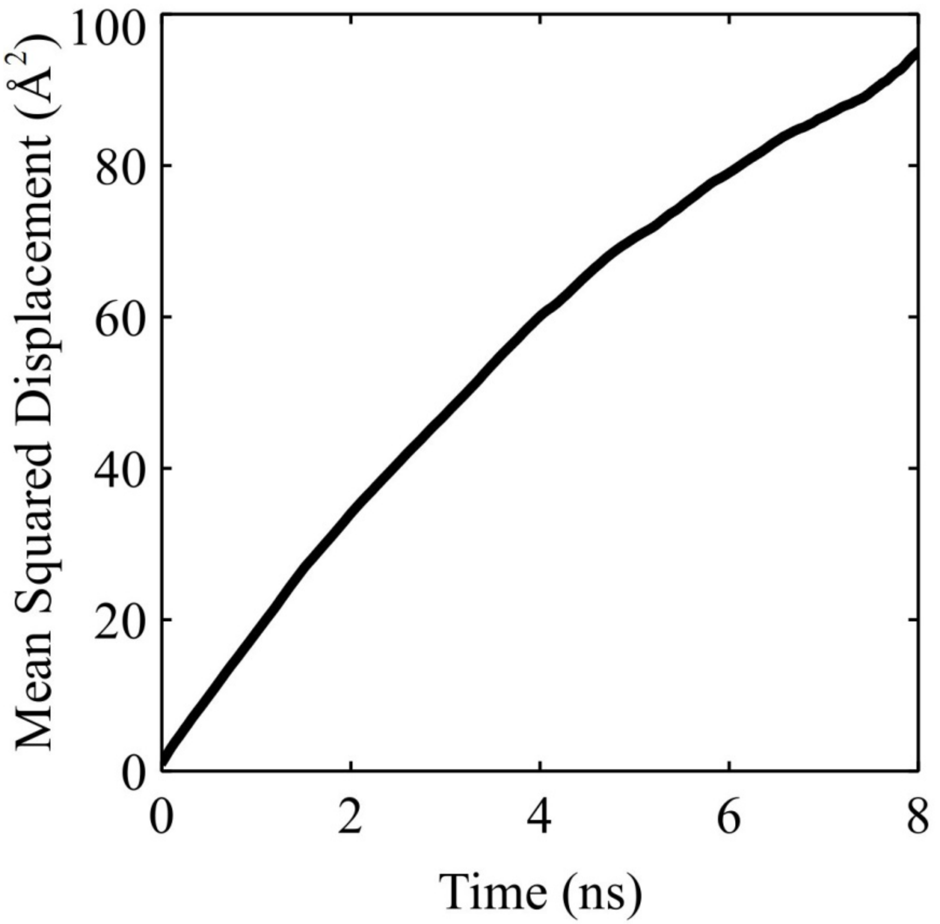

Figure S3. The calculated mean squared displacement (MSD) of the center of mass (COM) of CO_2 in α-Mg formate at a temperature of 253 K.

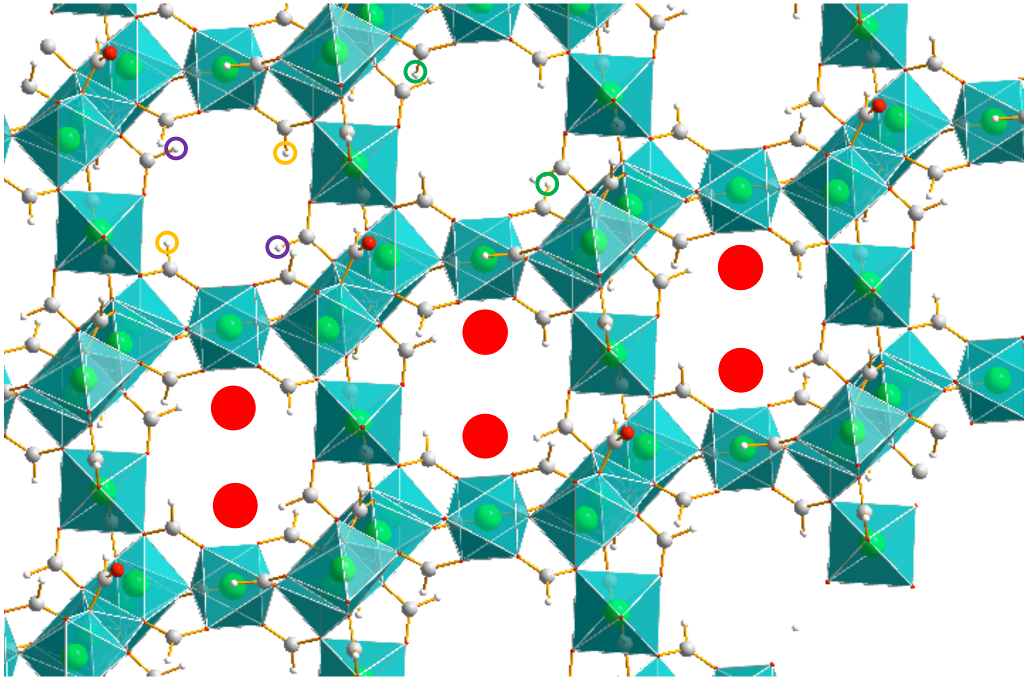

Figure S4. The extended crystal lattice of α-Mg formate, as viewed down the crystallographic *b* axis, is shown. There are six crystallographically unique hydrogen positions in this MOF, but only the three hydrogen atoms which protrude into the pore interior are shown here, highlighted by purple, yellow, and green circles. For clarity, the three types of hydrogen atoms are labeled within separate adjacent channels, although they all exist within the same channel. The red circles denote the CO_2 adsorption sites, and are only shown in three channels, but are present in all channels.

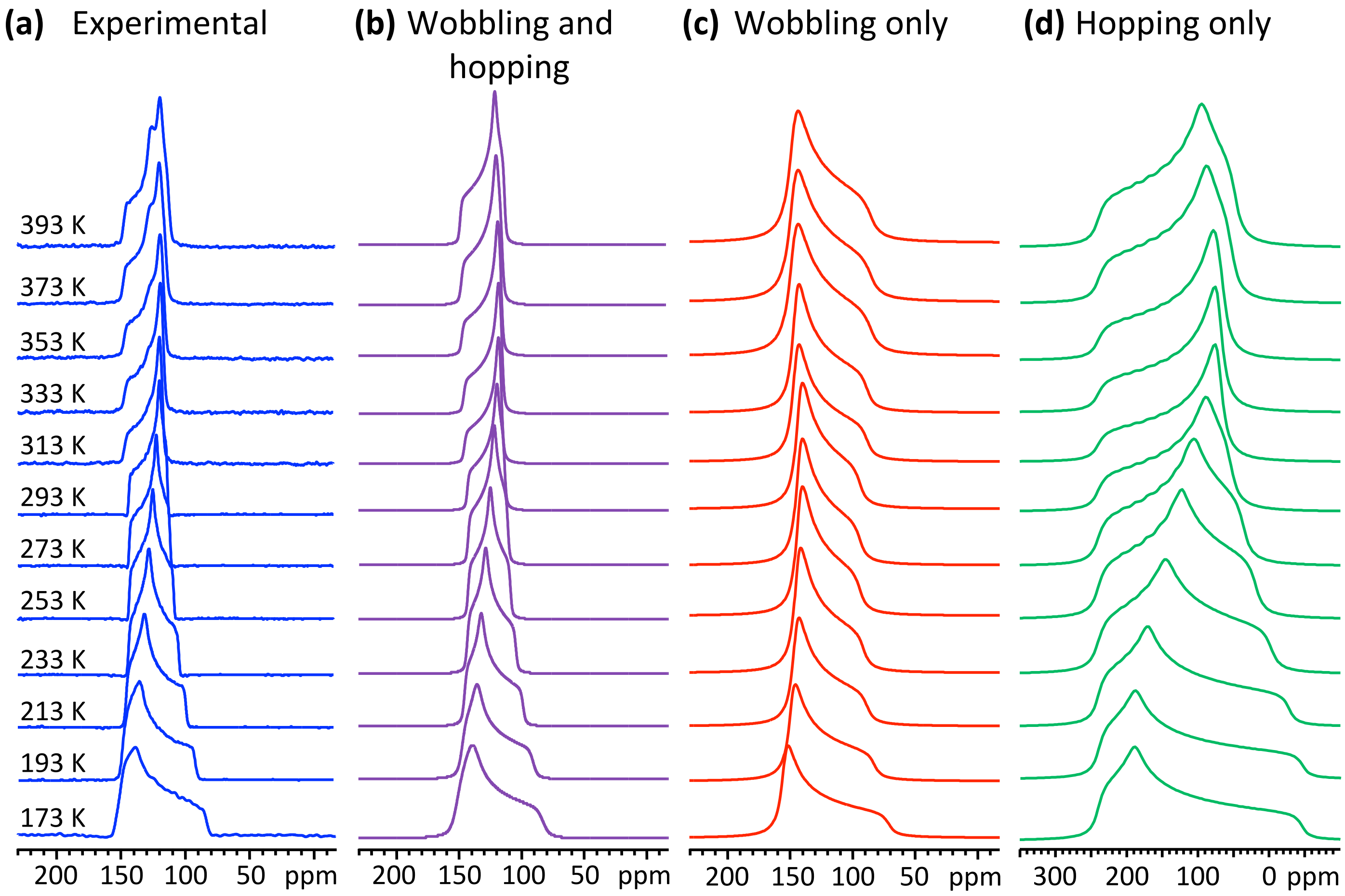

Figure S5. The experimental ^{13}C VT SSNMR spectra of CO_2-loaded α-Mg formate are shown in (a), along with simulations in (b), (c), and (d). In (b), motional simulations incorporating localized wobbling and non-localized twofold hopping are depicted; these match well with the experimental spectra in (a). In contrast, the simulated spectra shown in (c) that only consider localized wobbling of CO_2, as well as spectra in (d) that only incorporate the non-localized twofold hopping (d) of CO_2, are both poor matches to the experimental spectra. Note the difference in x-axis scale in (d).

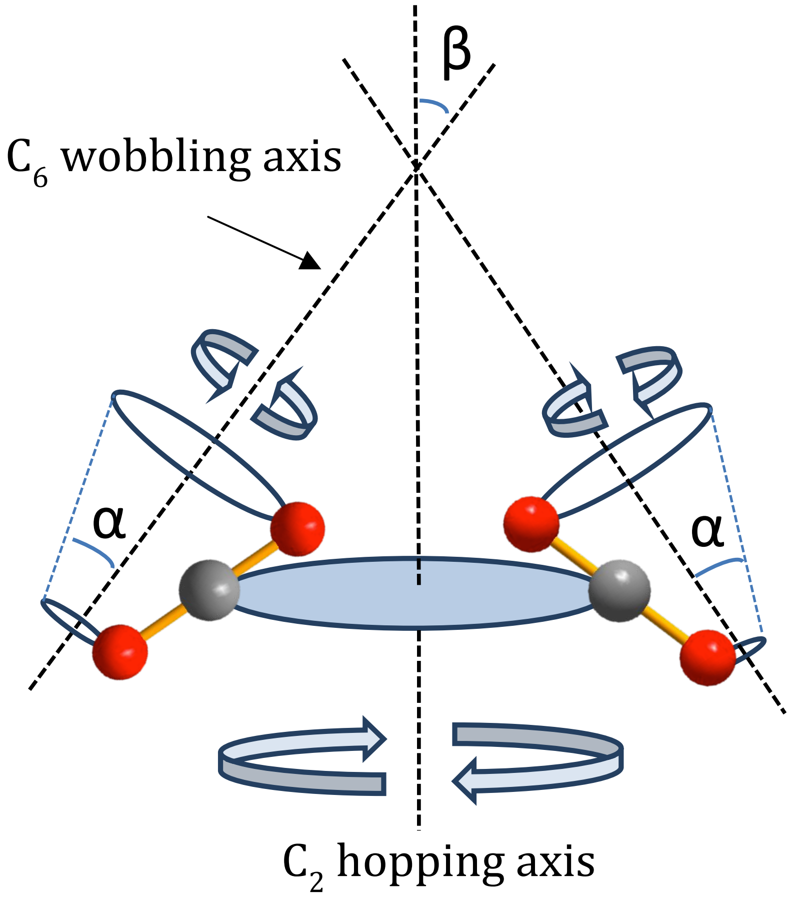

Figure S6. The dynamic motions of CO_2 molecules in the α-Mg formate MOF are illustrated. CO_2 participates in a localized wobbling through an angle of α, modeled by a C_6 sixfold rotation, along with a non-localized twofold (C_2) hopping through an equivalent angle β.

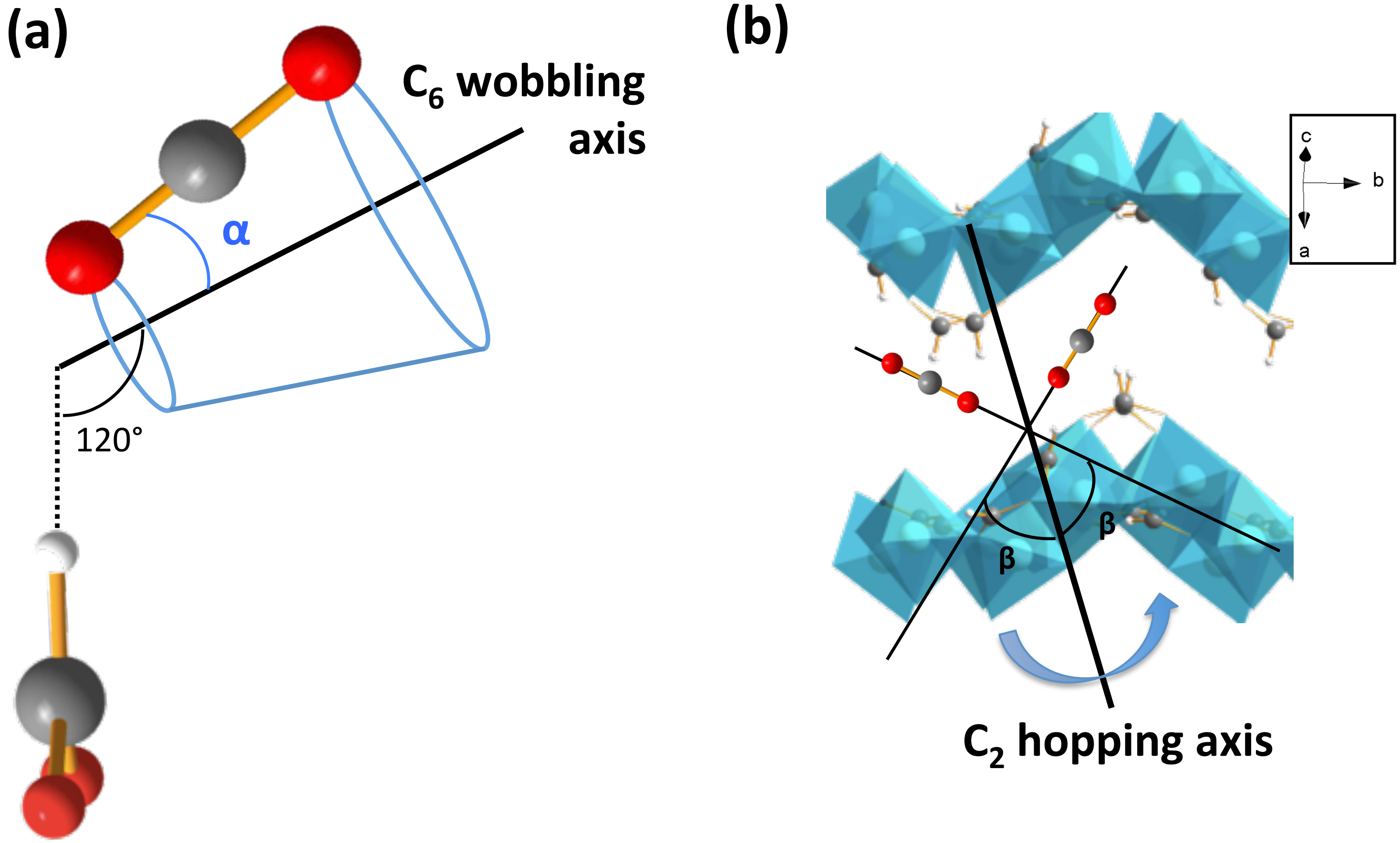

Figure S7. In (a), the localized C_6 wobbling of CO_2 through an angle of α about an individual hydrogen-based adsorption site within the pores of α-Mg formate is shown. The H(formate)…O-C(CO_2) angle is 120 ° and H(formate)…O(CO_2) distance is ca. 3.2 Angstroms, according to MD simulations (see main text). The illustration in (b) is a depiction of the non-localized C_2 hopping of CO_2 through an angle of β between hydrogen-based adsorption sites along the *b* axis of α-Mg formate.