Supplementary Material (ESI) for *PCCP*

# Supporting Information for: Molecular Dynamics Simulation of $^{13}$C NMR Powder Lineshapes of CO in Structure I Clathrate Hydrate

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## Viewing animations of the CO guest motion in sI large cages

The following four files are given as Supporting Information. Viewing these files with an appropriate molecular viewer can assist the reader in following some of the arguments given in the paper. A description of the four files follows:

1) *sI large cage 77 K.xyz* : The Cartesian coordinates of the 24 oxygen atoms of a sample sI large cage at 77 K over 2001 snapshots. The time increment between snapshots is 0.1 ps.
2) *sI CO guest 77 K.xyz* : The Cartesian coordinates of the 2 CO guest atoms of a sample sI large cage at 77 K over 2001 snapshots. The time increment between snapshots is 0.1 ps. This CO molecule belongs inside the cage given in the first file.
3) *sI large cage 220 K.xyz* : The Cartesian coordinates of the 24 oxygen atoms of a sample sI large cage at 220 K over 2001 snapshots. The time increment between snapshots is 0.1 ps.
4) *sI CO guest 220 K.xyz* : The Cartesian coordinates of the 2 CO guest atoms of a sample sI large cage at 220 K over 2001 snapshots. The time increment between snapshots is 0.1 ps. This CO molecule belongs inside the cage given in the third file.

The molecular viewer “VMD” is recommended to view these files, but other viewers could be used as well.

## Force field used in molecular dynamics simulations

Intermolecular potentials are taken as the sum of van der Waals (Lennard-Jones) and electrostatic point charge potentials centered on the carbon and oxygen atoms,

$$V(inter)=\sum_{i=1}^{N-1}\sum_{j>i}^{N}\left\{\ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right\}. \qquad \text{(S1)}$$

Point charges $q_i$ and $q_j$ located on the atomic nuclei $i$ and $j$ on different molecules are used to model electrostatic intermolecular interactions. Water molecules in the clathrate simulations are modeled by the extended simple point charge (SPC/E) model.[1] The carbon monoxide molecules are considered rigid and their Lennard-Jones parameters are taken from Palucha *et al*.[2] Lennard-Jones potential parameters between unlike atom-type force centers $i$ and $j$ are calculated with the Lorentz-Bertholet combination rules, $\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$ and $\sigma_{ij} = (\sigma_{ii}+\sigma_{jj})/2$. The intermolecular potential parameters used in the simulations are given in Table S1. The O atom of CO is seen to have a stronger LJ potential than the C atom.

References:

[1] H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J. Phys. Chem.*, 1987, **91**, 6269-6271.

[2] S. Palucha, Z. Gburski and J. Biesiada, *J. Molecular Structure,* 2004, **704**, 269-273.

**Table S1.** Atomic charges and Lennard-Jones interaction parameters for SPC/E water and carbon monoxide used in the MD simulations.

| Atoms (assignment) | $q(e)$ | $\sigma_{\mathrm{ii}}$ / Å [a] | $\varepsilon_{\mathrm{ii}}$ /kJmol$^{-1}$ [a] |
|---|---|---|---|
| O (water) | -0.8476 | 3.166 | 0.6502 |
| H (water) | +0.4238 | 0.000 | 0.0000 |
| C | +0.0223 | 3.55 | 0.3089 |
| O | -0.0223 | 2.95 | 0.5120 |

[a] The intermolecular potential parameters between unlike atoms are determined from combination rules.

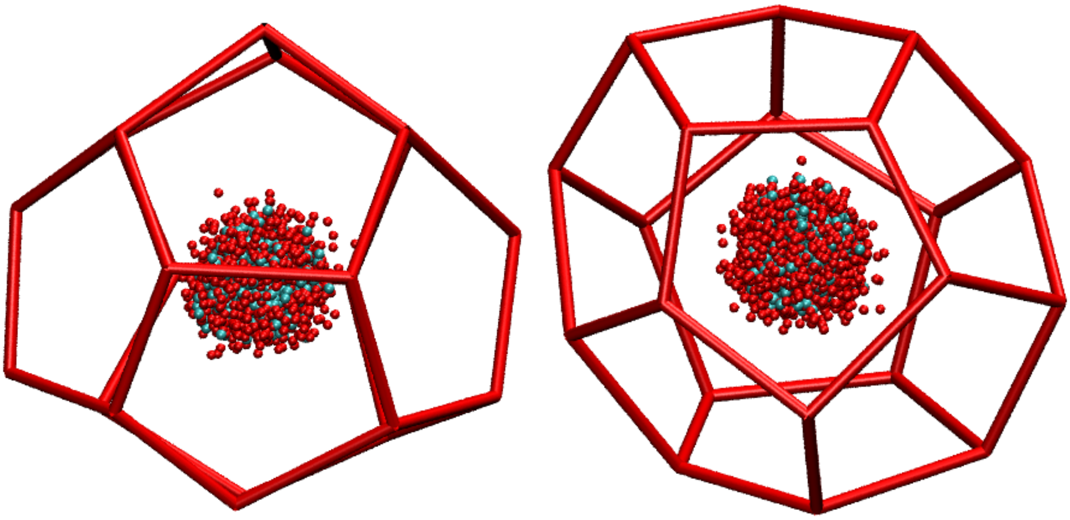

**Figure S1.** The distribution of the CO molecule at different times in a typical sI clathrate hydrate small cage viewed from two directions from the simulation at 220 K. The distribution of the CO molecule is isotropic with respect to orientation of the molecule. The oxygen atoms (red spheres) primarily face towards the clathrate cage wall.

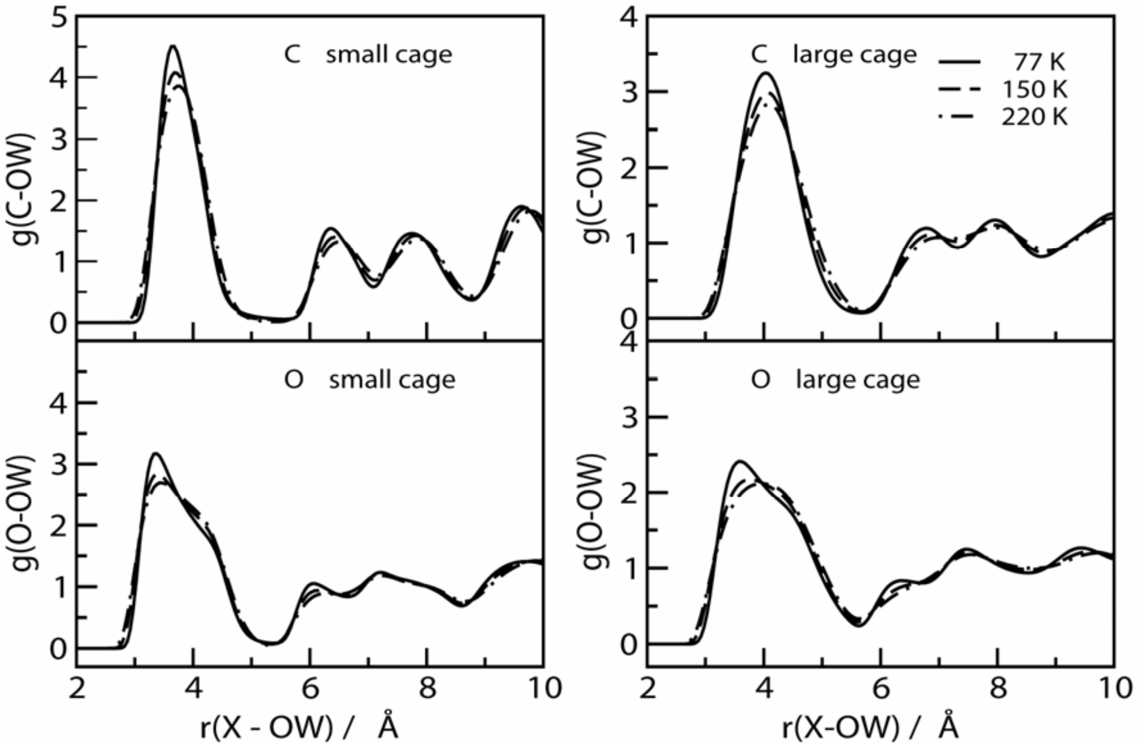

**Figure S2.** The radial distribution functions for the C and O atoms of CO with respect to the cage water oxygen atoms OW for CO in the small cages (left panels) and CO in the large sI cages (right hand panel). RDFs at the three simulation temperatures are given. Note that the first peak in the RDF for the O atoms of CO in the large cages is between 3.5-4.0 Å. The peak in the RDF of the C atom of CO in the large cages is spaced further out showing that the CO molecule is associated through its O atom to the cage. The RDFs for the O and C atoms of $CO_2$ guests in the large cages with the OW atoms are shown in Figure S3.

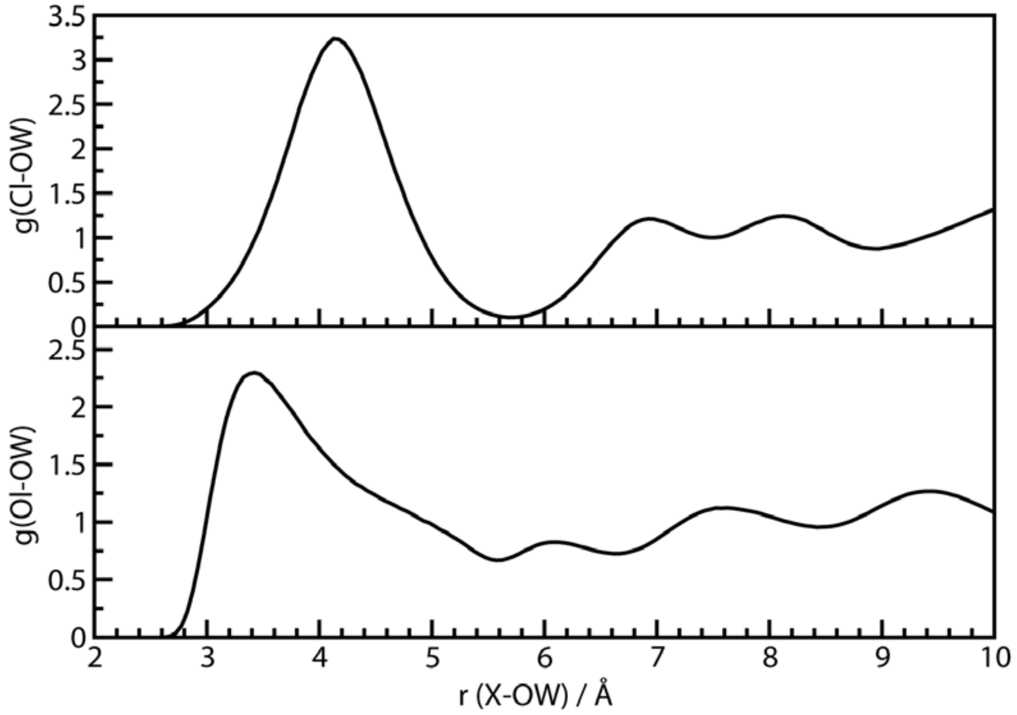

**Figure S3.** The radial distribution functions for the C and O atoms of $CO_2$ with respect to the cage water oxygen atoms OW for $CO_2$ in the large sI cages at 238 K. The RDF for the O atoms of $CO_2$ in the large cages has a peak at ~3.4 Å.

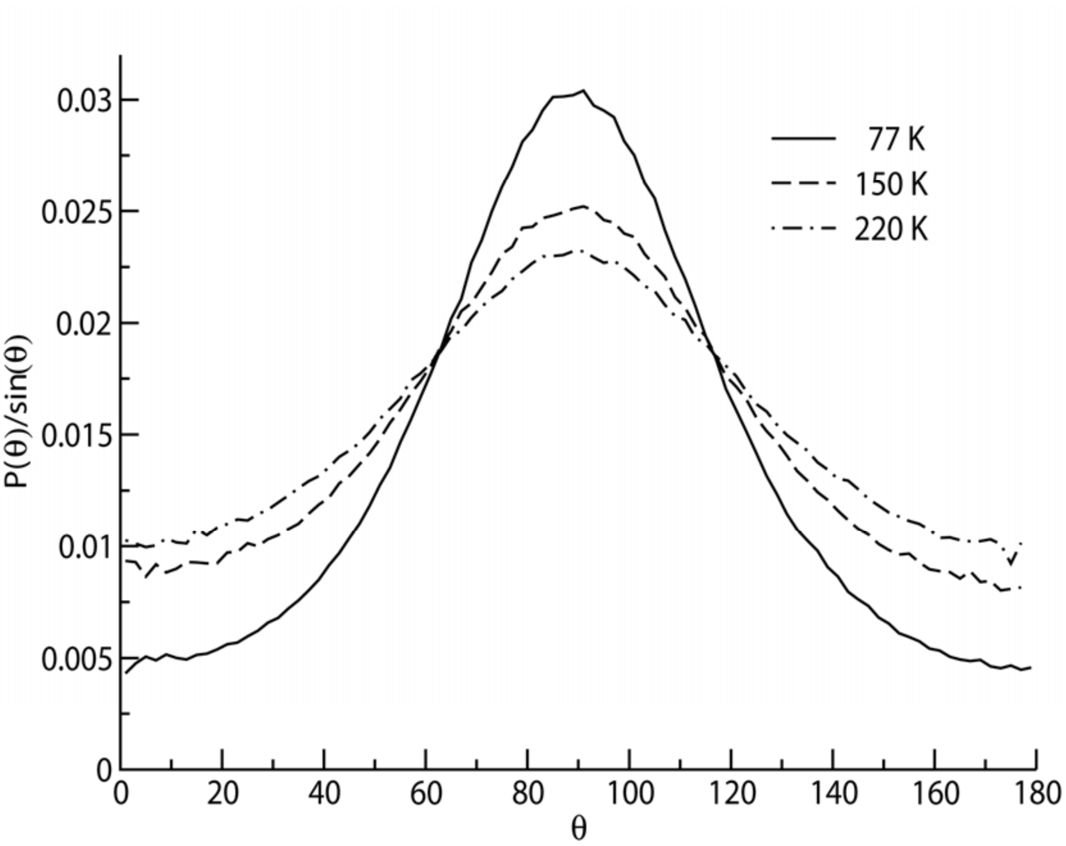

**Figure S4.** The angular probability distribution function $P(\theta;T)/\sin(\theta)$ calculated from Figure 3. The polar angle distributions are not randomized, even at the high temperature limit of stability of the clathrate.

## Dynamic behavior of CO in the sI clathrate cages

The dynamic behavior and the microscopic motion of the guests can be studied by calculating the mean-square displacement (MSD), $\Delta|\mathbf{r}(t)|^2$, the velocity autocorrelation function (VACF), $C_v(t)$, and the orientational autocorrelation function (OACF), $M(\mathrm{t})$, for the CO with molecular dynamics simulations. The MSDs for the C atom of CO molecule in small and large cages at three temperatures are shown in Figure S5. As expected, the CO molecules in the small cages have smaller ranges and higher frequencies of motions than the CO molecules in the large cages at each temperature. For comparison, we also examine the MSDs from the molecular dynamics simulations of $CO_2$ in the sI clathrate. Shown in the lower half of Figure S5 are the MSDs for the C atom of the $CO_2$ molecule in the sI small and large cages at 77 K. We can see that the larger $CO_2$ molecule has much smaller rattling motion amplitude in both small and large cages than CO. Although some of the changes with temperature in the NMR lineshape of $CO_2$ and CO in the sI clathrates may appear superficially similar, these two guest species have significantly different regimes of motion.

The VACFs for the C atom of CO molecule in small and large cages and their Fourier transform at three temperatures are shown in Figure S6. The VACFs give a general indication of the rattling motion of the guests in the small and large cages. Once again, as expected, the motion of the CO molecules in the small cages has a higher frequency. As expected, the motion of the CO molecules in the small cages has a higher frequency. The Fourier transform of the VACF shows that the rattling motion inside of the small cage has a distinct period of ~0.5 ps. The motion in the large cages is seen to be much less regular and consists of a superposition of a number of vibrational motions with a period range of ~0.5 – ~1.5 ps.

The VACFs for the C atom of $CO_2$ in the small and large sI clathrate hydrate cages at 77 K along with their Fourier transform are given in Figure S7 for comparison with the CO clathrates. As expected, the VACF for $CO_2$ in the small cages has a smaller period (higher frequency) than $CO_2$ in the large cages. The oscillations in the VACF of $CO_2$ are severely damped compared to those of CO and have much smaller amplitudes. This once again shows that the two guests have different motion regimes in the sI clathrate cages.

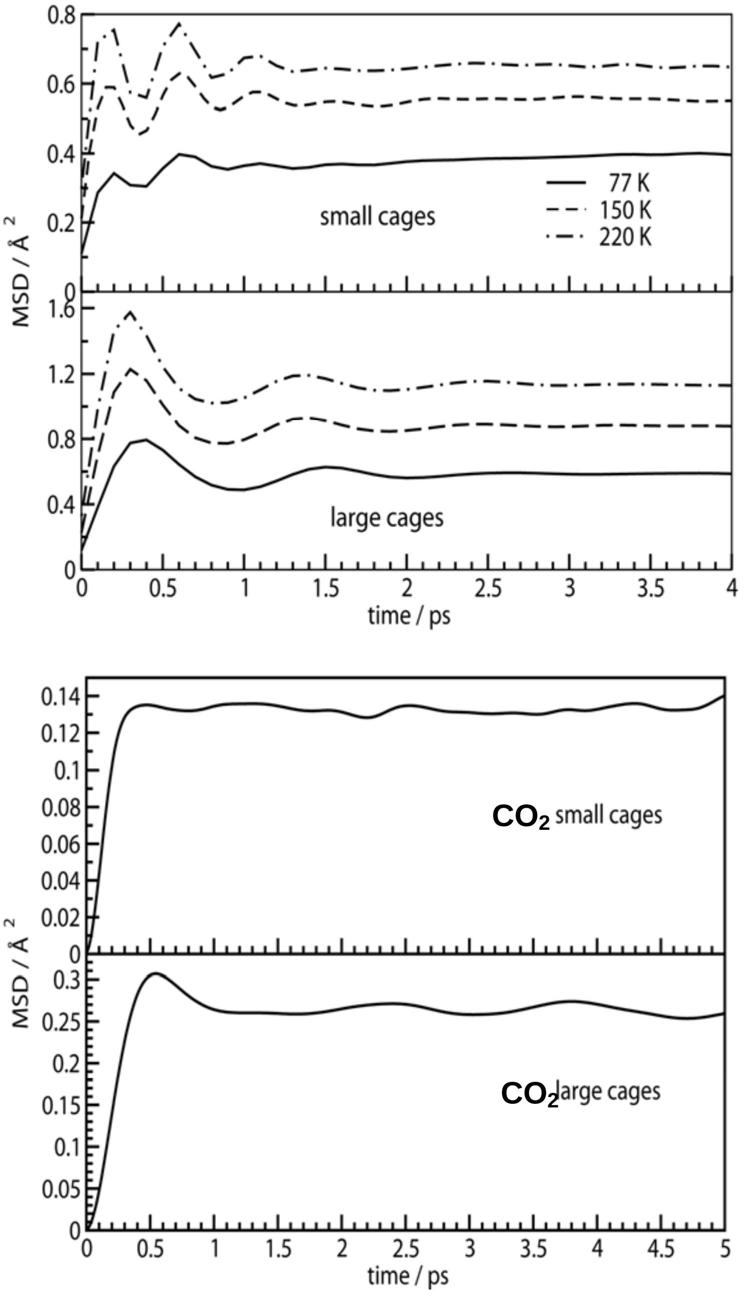

**Figure S5.** The mean-square displacement (MSD) of the C atom of CO in small and large cages of sI clathrate hydrate at three temperatures and 1 bar pressure and $CO_2$ at 77 K and 1 bar.

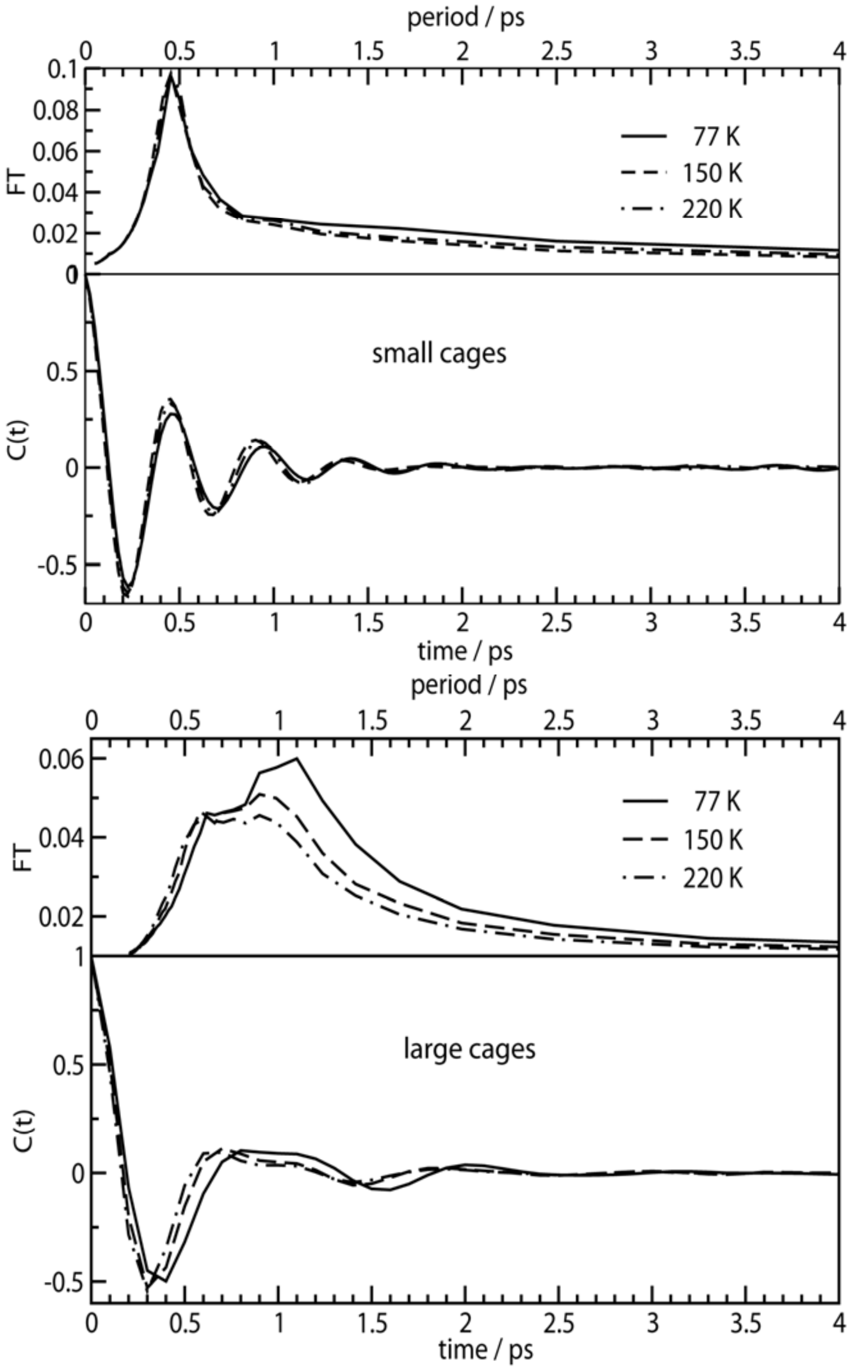

**Figure S6.** The calculated velocity autocorrelation functions (VACFs) and the Fourier transform of the VACFs of the C atom of CO in small and large cages of sI clathrate hydrate at three temperatures and 1 bar pressure.

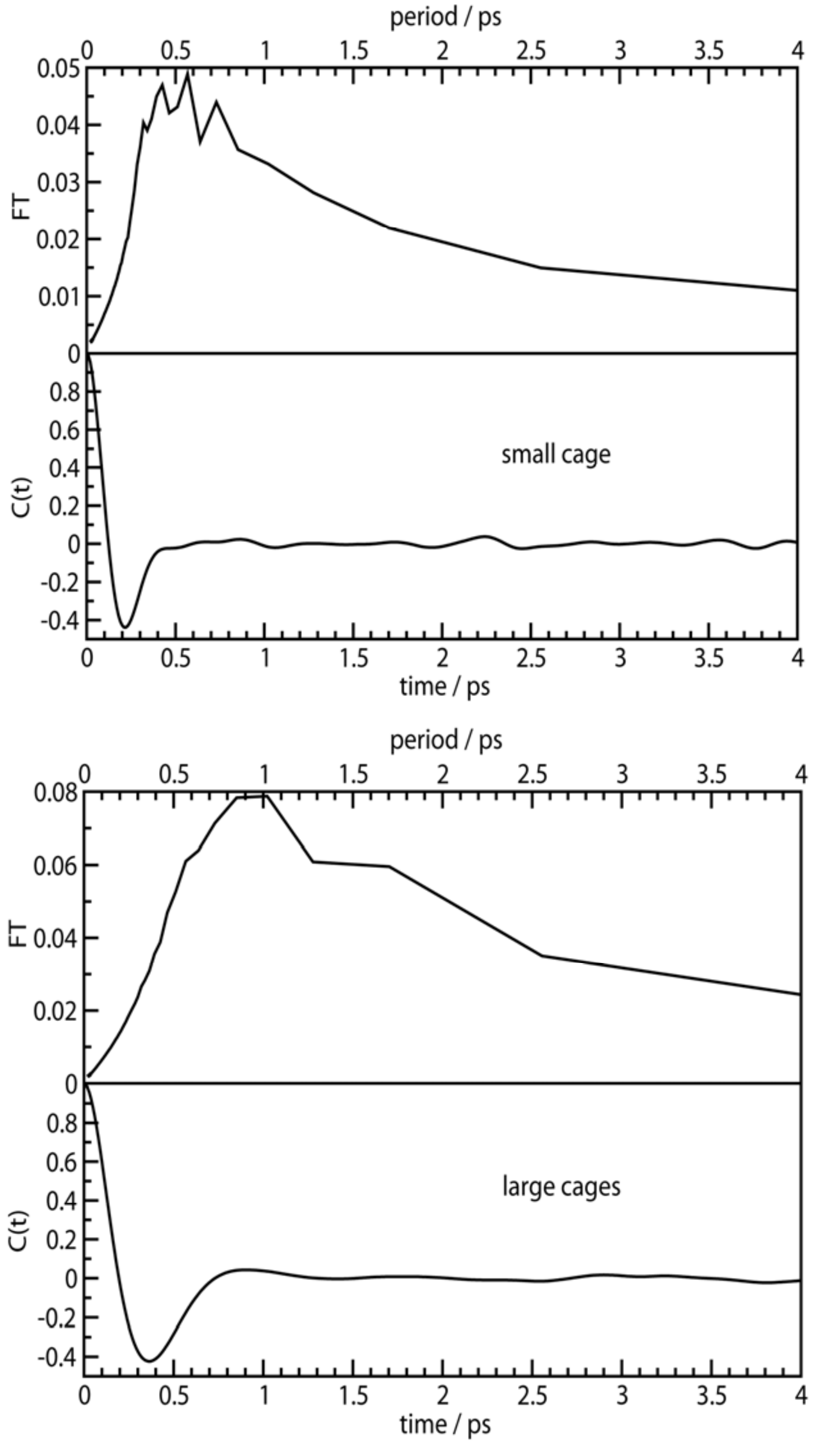

**Figure S7.** The calculated velocity autocorrelation functions (VACFs) and the Fourier transform of the VACFs of the C atom of $CO_2$ in small and large cages of sI clathrate hydrate at 77 K and 1 bar pressure.