## Molecular Storage of Ozone in a Clathrate Hydrate: An Attempt at Preserving Ozone at High Concentrations

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## Supporting Information S1: Experimental data of hydrate and gas-phase compositions

The experimental data of the ozone content in the hydrate formed in each hydrate-forming experiment are summarized in Table S1. A counterpart to this set of "hydrate-side" data is given in Table S2; it is a set of "gas-phase-side" composition data obtained by sampling the gas mixture in the reactor at the end of each hydrate-forming process. It should be noted that, due to the insufficient reproducibility of the gas-exchange operations during each hydrate-forming experiment, the actual compositions measured with individual gas-mixture samples were erratically deviating from the corresponding *nominal* composition indicated on the leftmost column of the table. Because the hydrate formation had almost ceased at the time of such gas sampling in every hydrate-forming experiment, we can reasonably assume that the ozone content of each hydrate specified in Table S1 is nearly in a thermodynamic equilibrium relation to the corresponding gas-phase composition specified in Table S2.

The  $x_{CO3,init}$  and  $X_{O3}$  data given in Tables S1 and S2 were used to prepare Fig. 3 and 4 in the main body of this paper. If we replace  $X_{O3}$  on the abscissa in Fig. 4 with  $p_{O3}$ , the partial pressure of ozone in the gas phase, we have the  $x_{CO3,init}$  versus  $p_{O3}$  diagram shown in Fig. S1. Although the  $x_{CO3,init}$  data points for each level of the system pressure p seem to be correlated with  $p_{O3}$ , we note a systematic shift in the data points depending on p. Obviously, all the data points are better correlated with  $X_{O3}$  (see Fig. 4) rather than with  $p_{O3}$ .

**Table S1.** Summarized iodometric data of  $x_{CO3,init}$ , the mass fraction of ozone in the hydrate formed from an  $O_3 + O_2 + CO_2$  gas mixture with a prescribed  $(O_3 + O_2)$ -to- $CO_2$  molar ratio under a nearly constant system pressure *p*. Each  $x_{CO3,init}$  value listed here is an arithmetic mean of the values determined by three independent measurements. Note that the " $O_3 + O_2 : CO_2$ " values indexed on the leftmost column represent the *nominal* feed-gas compositions, instead of the actually measured compositions.

$O_3 + O_2 : CO_2$	$x_{\rm O3,init} \times 100$			
	<i>p</i> = 2.0 MPa	<i>p</i> = 2.5 MPa	<i>p</i> = 3.0 MPa	
1:9	0.318	0.215	0.217	
2:8	0.472	0.373	0.575	
3:7	0.879, 0.640	0.715	0.695	
4:6	0.791	0.783	0.912	

**Table S2.** Summarized gas-chromatographic data of mole fractions of  $O_3$ ,  $O_2$  and  $CO_2$  in the gas phase filling the reactor at the end of each hydrate-forming experiment.

$O_3 + O_2 : CO_2$	<i>p</i> / MPa	$X_{\rm O3}$	$X_{O2}$	$X_{\rm CO2}$
1:9	2.0	0.007	0.130	0.863
	2.5	0.006	0.079	0.915
	3.0	0.008	0.076	0.916
2:8	2.0	0.015	0.182	0.803
	2.5	0.010	0.171	0.819
	3.0	0.013	0.164	0.823
3:7	2.0	0.015	0.282	0.703
	2.0	0.013	0.331	0.657
	2.5	0.018	0.253	0.730
	3.0	0.018	0.273	0.709
4:6	2.0	0.017	0.393	0.590
	2.5	0.017	0.433	0.551
	3.0	0.021	0.409	0.570



**Figure S1.** The initial ozone fraction (mass basis) in the formed hydrate,  $x_{O3,init}$ , versus  $p_{O3}$ , the partial pressure of ozone in the gas phase filling the reactor at the end of each hydrate-forming experiment. The legend inserted in the graph indicates the system pressure *p* during each hydrate-forming operation. The error bar for each data point represents the uncertainty of the ozone-fraction measurement by iodometry.