Supplementary Information: O_2 Formation in Cold Environments

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The supplementary information provides additional information about the energy conservation of various implementation of reactive dynamics implemented in the main report"

S1 KKY simulations

The KKY model was implemented in CHARMM c41. The implementation of the code and parameters are those used in previous work.[1] To validate the implementation, a 2 ns NVE simulation was carried out and the fluctuation in the total energy is reported in Figure S1. The normal mode frequencies from the KKY model and from experiment also agree quite favourable, see Table S1

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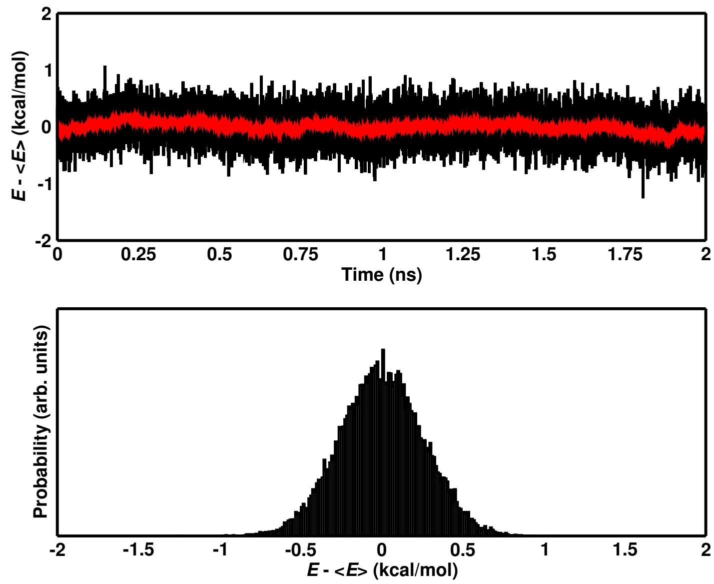

Figure S1: KKY with RKHS or Morse for O_2 Top: Total Energy time series for 2 ns simulation of relaxed O_2 with the flexible H_2O. The energy is conserved within 1 kcal/mol, and presents a Gaussian Shaped distribution (bottom panel).

MODE	NIST Database (cm^{-1})	KKY (cm^{-1})	Difference (cm^{-1})
Symmetric Stretch	3657	3682	+25
Antisymmetric Stretch	3756	3720	-36
Bending	1595	1593	-2

S2 Exponential and Stretched Exponential Fits

Additional fitts of the relaxation curves to exponential and stretched exponential models are summarized in the following.

References

(1) Plattner, N.; Meuwly, M. Atomistic Simulations of CO Vibrations in Ices Relevant to Astrochemistry. *ChemPhysChem* **2008**, *9*, 1271–1277.

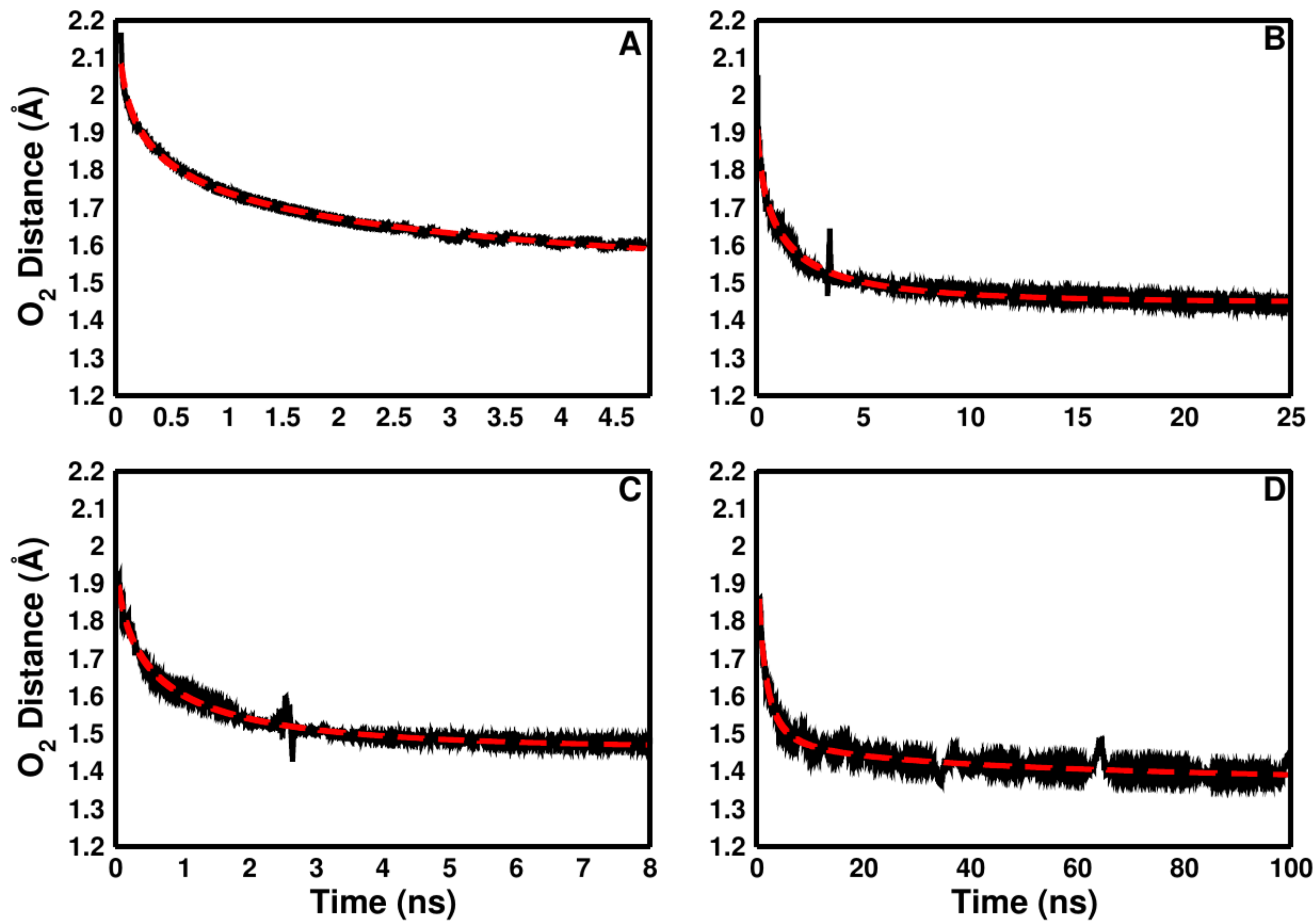

Figure S2: Vibrational relaxation for O_2 recombination inside the cavity (panel A) and on the surface of ASW (panels B to D). The 16 simulations in panel A were run with [TIP3P/RKHS]. Fitting to a double exponential decay gives relaxation times $\tau_1 = 0.5$ ns and $\tau_2 = 15$ ns. Simulations in panels B to D were run with [TIP3P/RKHS] ($\tau_1 = 1.1$ ns and $\tau_2 = 83.4$ ns), [KKY/RKHS] ($\tau_1 = 0.7$ ns and $\tau_2 = 20.7$ ns) and [TIP3P/Morse] ($\tau_1 = 3.0$ ns and $\tau_2 = 206.9$ ns). The right-hand $y-$axis label reports the vibrational quantum number from solving the 1d-Schrödinger equation using LEVEL.[2] After 20 to 80 ns of simulation time the O_2 molecule is still in a state corresponding to $v = 16$ to 20.

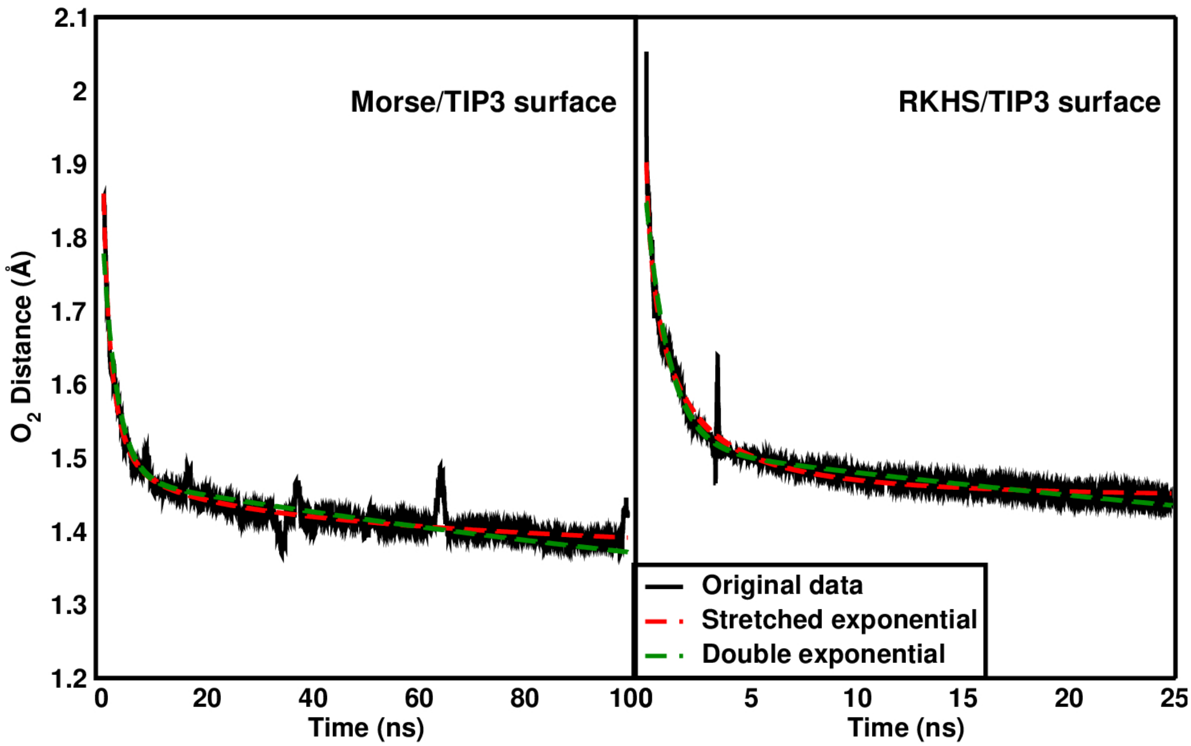

Figure S3: Comparison between the stretched exponential (red) and double exponential (green) decay between for simulations with [TIP3P/Morse] (right) and [TIP3P/RKHS] (left). A stretched exponential better captures the early time decay and the flattening out at long times. The relaxation times corresponding to this data is reported in Table 1.

(2) Roy, R. J. L. LEVEL: A computer program for solving the radial Schrdinger equation for bound and quasibound levels. *J. Quant. Spectrosc. Radiat. Transfer* **2017**, *186*, 167 – 178.