

SUPPORTING INFORMATION

First Principles Monte Carlo Simulations of Reaction Equilibria in Compressed Vapors

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Identification of Molecules

In the RxFPMC (reactive first principles Monte Carlo) approach, molecules are simply aggregates of atoms. Thus, a set of criteria is needed to determine speciation (composition in terms of aggregates/molecules). Here we follow the Stillinger approach [Stillinger, F. H. *J. Chem. Phys.* **1963**, *38*, 1486–1494] and use a geometric cut-off criterion to determine whether any two atoms belong to the same aggregate. Such a criterion does not restrict the size of aggregates (i.e., the number of atoms in a molecule). The N-N, O-O, and N-O radial distribution functions (RDFs) for five N:O ratios are shown in **Figure S1**. The positions of the first peak are 1.08, 1.23, and 1.12 Å for the N-N, O-O, and N-O RDFs, respectively. The first minimum for the O-O RDFs is found at 1.60 Å. At this location, the N-N and N-O RDFs yield average values for the five compositions that are about 0.0011 and 0.06, respectively. Thus, 1.60 Å is a suitable value that can be applied as the geometric cutoff criterion for N-N, N-O, and O-O atom pairs.

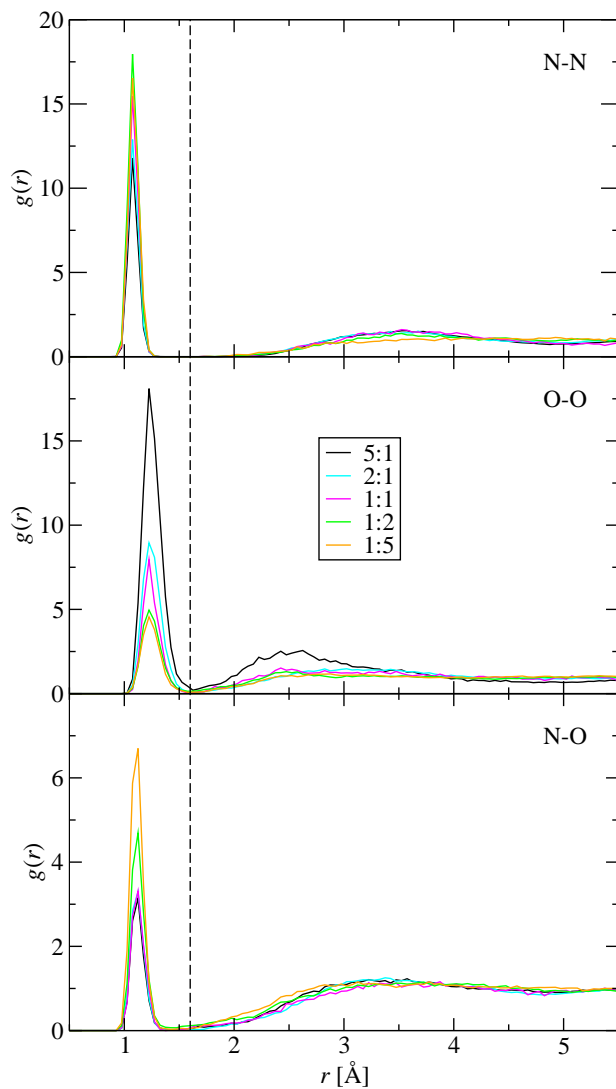


Figure S1. Nitrogen–nitrogen (top), oxygen–oxygen (middle), and nitrogen–oxygen (bottom) radial distribution functions obtained for systems with N:O ratios of 5:1 (black), 2:1 (cyan), 1:1 (magenta), 1:2 (green), and 1:5 (orange). The vertical dashed lines show the cutoff criterion for aggregation at $r = 1.60 \text{ \AA}$.

Numerical Values for Speciation

Table S1. Equilibrium molar fractions for the five different species observed in the RxFPMC simulations (see Figures 2 and 3). The subscripts for the RxFPMC results denote the 95% confidence intervals obtained from 32 independent simulations at each composition.

The RxMC results are taken from Smith and Triska [Smith, W. R.; Triska, B. *J. Chem. Phys.* **1994**, *100*, 3019–3027] and the subscripts denote the precision of the data quoted by these authors.

The thermochemical distributions are obtained using the Cheetah 8.0 thermochemical code which employs an equation of state based on $\exp-6$ and dipolar interactions between molecular gas products [Bastea, S.; Fried, L. E. *J. Chem. Phys.* **2008**, *128*, 174502; Bastea, S.; Fried, L. E.; Chemical Equilibrium Detonation, in Shock Wave Science and Technology Reference Library, Vol. 6, pp. 1–31, edited by F. Zhang (Springer, Berlin; 2012); Bastea, S.; Fried, L. E.; Glaesemann, K. R.; Howard, W. M.; Kuo, I. F. W.; Souers, P. C.; Vitello, P. A.; Cheetah 8.0 User's Manual, LLNL-SM-677152 (Lawrence Livermore National Laboratory, 2015)]. The parameters for the equation of state utilized in Cheetah are obtained by fitting to available experimental data as well as simulation results, e.g., for dioxygen about 95% of the data points are sourced from experimental measurements.

N:O ratio	Method	NO	O ₂	N ₂	NO ₂	N ₂ O
5:1	RxMC	0.1785 ₄	0.0774 ₄	0.7441 ₄	—	—
	Cheetah	0.1892	0.0696	0.7363	0.0008	0.0040
	RxFPMC(BLYP)-96	0.162 ₄	0.085 ₂	0.746 ₂	0.001 ₁	0.006 ₂
	RxFPMC(BLYP)-192	0.157 ₁₀	0.090 ₅	0.749 ₅	0.000 ₁	0.004 ₃
2:1	RxMC	0.2522 ₅	0.2072 ₅	0.5406 ₅	—	—
	Cheetah	0.2939	0.1816	0.5146	0.0028	0.0069
	RxFPMC(BLYP)-96	0.232 ₃	0.209 ₂	0.554 ₂	0.003 ₂	0.002 ₁
	RxFPMC(BLYP)-192	0.229 ₈	0.216 ₄	0.551 ₄	0.002 ₂	0.002 ₂
1:1	RxMC	0.2755 ₄	0.3623 ₄	0.3623 ₄	—	—
	Cheetah	0.3383	0.3242	0.3233	0.0061	0.0080
	RxFPMC(BLYP)-96	0.279 ₂	0.351 ₂	0.364 ₂	0.004 ₂	0.002 ₁
	RxFPMC(BLYP)-192	0.269 ₉	0.358 ₅	0.366 ₅	0.004 ₃	0.003 ₂
	RxFPMC(M06)	0.275 ₃	0.354 ₃	0.372 ₃	0.004 ₂	0.003 ₂
	RxFPMC(rVV10)	0.285 ₃	0.346 ₂	0.368 ₂	0.006 ₂	0.002 ₂
1:2	RxMC	0.2543 ₄	0.5395 ₄	0.2062 ₄	—	—
	Cheetah	0.3199	0.4993	0.1650	0.0091	0.0065
	RxFPMC(BLYP)-96	0.285 ₃	0.517 ₂	0.184 ₂	0.010 ₂	0.004 ₁
1:5	RxMC	0.1810 ₄	0.7428 ₄	0.0762 ₄	—	—
	Cheetah	0.2149	0.7200	0.0531	0.0089	0.0027
	RxFPMC(BLYP)-96	0.241 ₅	0.705 ₃	0.046 ₂	0.006 ₁	0.002 ₁

Reaction Energies

As validation for the implementation of the different density functionals and of the pseudopotential approach utilized in the RxFPMC simulations within CP2K, we calculate compound energies for N₂, O₂, and NO (in singlet, triplet, and doublet states, respectively) and the resulting reaction energy, ΔE , using isolated molecules in a periodic box with a linear dimension of 12.5 Å (i.e., similar to the average box size for the RxFPMC simulations) and a cutoff at 600 Ry. We have validated that removing the interactions with periodic images via the Martyna-Tuckerman approach leads to changes in the reaction energies that are less than 0.01 kJ/mol. **Table S1** compares these data to all-electron calculations for isolated molecules. In all cases, the pseudopotential calculation yields a slightly larger ΔE value than the all-electron calculations. The deviations in ΔE values for pseudopotential and all-electron approaches are 0.3, 2.8, and 1.3 kJ/mol for the BLYP, VV10, and M06 functionals. Furthermore, the order of the ΔE values is preserved with VV10 yielding the least endothermic reaction and M06 yielding the most endothermic reaction. The corresponding $\Delta\Delta E$ values between most and least endothermic are only 5.0 and 3.5 kJ/mol for the pseudopotential and all-electron calculations.

Table S2. Compound energies (in Hartree) and reaction energy (in kJ/mol) for the N₂ + O₂ \rightleftharpoons 2 NO reaction using different functionals and software packages [Gaussian 09, Revision E.01, Frisch, M. J. *et al.*, Gaussian, Inc., Wallingford CT, 2009; Q-Chem 4, Shao, Y. *et al.*, *Mol. Phys.* **2015**, *113*, 184–215].

Functional/Software	N ₂	O ₂	NO	ΔE
BLYP/CP2K	-19.863206	-31.883089	-25.838632	+181.2
BLYP/Gaussian	-109.550246	-150.369648	-129.925504	+180.9
M06/CP2K	-18.702868	-30.235845	-24.434161	+184.8
M06/Gaussian	-109.494500	-150.294784	-129.859976	+182.0
rVV10/CP2K	-19.894733	-31.906656	-25.866448	+179.8
VV10/QChem	-109.724915	-150.576013	-130.116469	+178.5

Analysis of Local Spin Densities

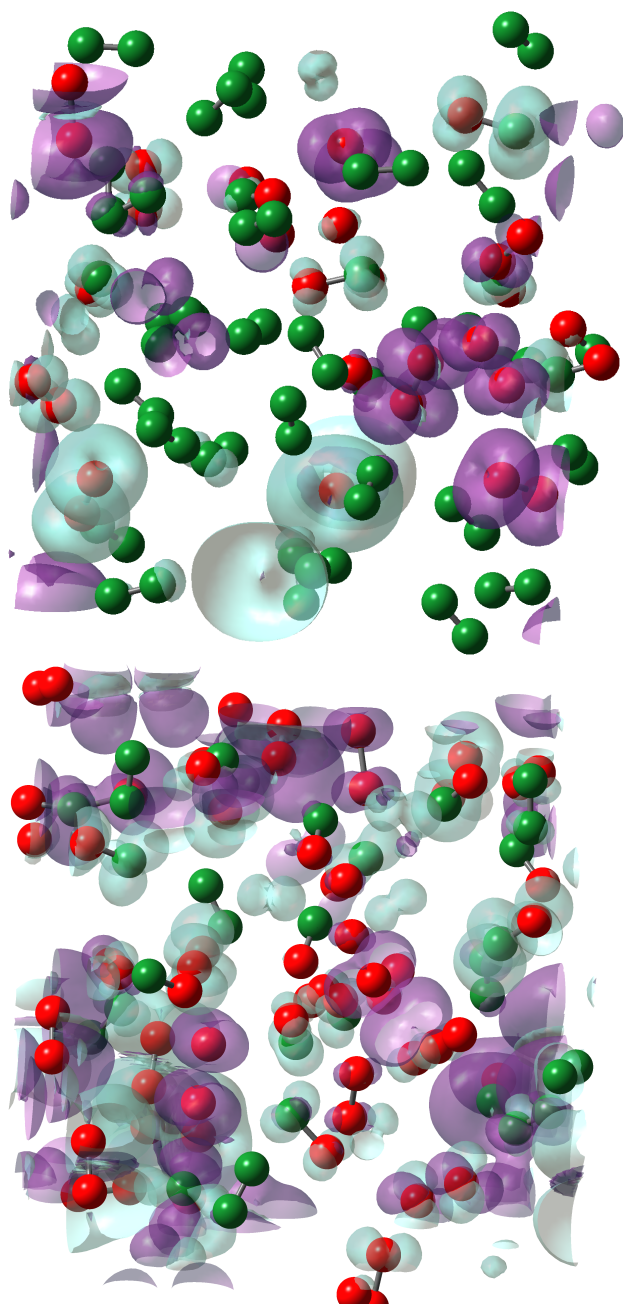


Figure S2. Snapshots of 96-atom systems with N:O ratios of 2:1 (top) and 1:2 (bottom). Nitrogen and oxygen nuclei are shown as green and red spheres, and the purple and cyan isosurfaces represent local spin density (LSD) of different signs. The LSD is obtained from an electron spin analysis within CP2K using spin-polarized (unrestricted) KS-DFT [Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200–1211; Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, 23, 5048–5079.]

Numerical Values for Bond Lengths

Table S3. Average bond lengths [in Å] for NO, O₂, and N₂ molecules calculated from the RxFPMC simulations for the five compositions and for isolated molecules. The subscripts for the RxFPMC results denote the 95% confidence intervals obtained from 32 independent simulations at each composition.

System	NO	O ₂	N ₂
isolated	1.1901 ₇	1.2655 ₇	1.1144 ₅
5:1	1.155 ₂	1.294 ₂	1.112 ₁
2:1	1.154 ₁	1.291 ₂	1.111 ₁
1:1	1.153 ₂	1.286 ₁	1.112 ₁
1:2	1.152 ₁	1.284 ₁	1.112 ₁
1:5	1.147 ₁	1.282 ₁	1.117 ₂