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

Supporting Information

N_2O_5 at Water Surfaces: Binding Forces, Charge Separation, Energy Accommodation and Atmospheric Implications

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Figure S1 presents the calculated structure of the C_2 and Cs isomers of N_2O_5 at the ωB97X-D/aug-cc-pVTZ level of theory, in comparison to experimental values[1,2]. In **Figure S2**, we present the minimum structures for the $N_2O_5 \cdot (H_2O)_n$ clusters for n = 1, 2, 3, 4, and 6. For a given n, the structure on the left corresponds to the optimization of a structure where the N_2O_5 had initially C_2 symmetry, and the structure on the right, to a structure where the N_2O_5 had initially C_s symmetry. We list as well the calculated relative energy and BSSE-corrected binding energy for each structure. The squared structure for a given n is the one found to be the most stable. Note that for n = 2, the two minima are found to be almost degenerate. In **Table TS1** we collect the partial charges on the NO_2 fragment for each cluster. In **Table TS2** we provide a QTAIM[3,4] analysis of the hydrogen bonds and an estimation of the hydrogen bond energy according to Espinosa[5]. The analysis was done using AIMAll (Version 17.11.14)[6].

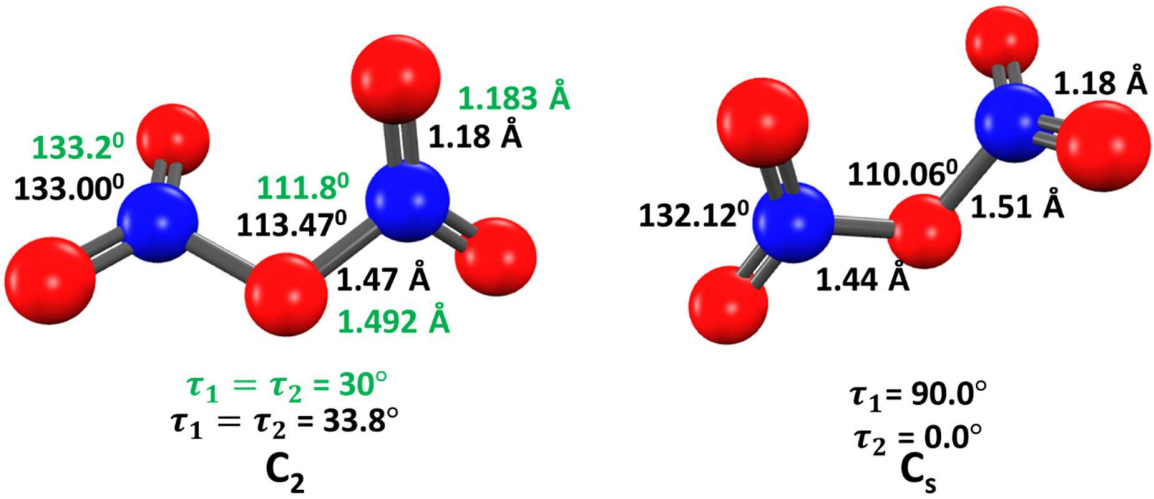
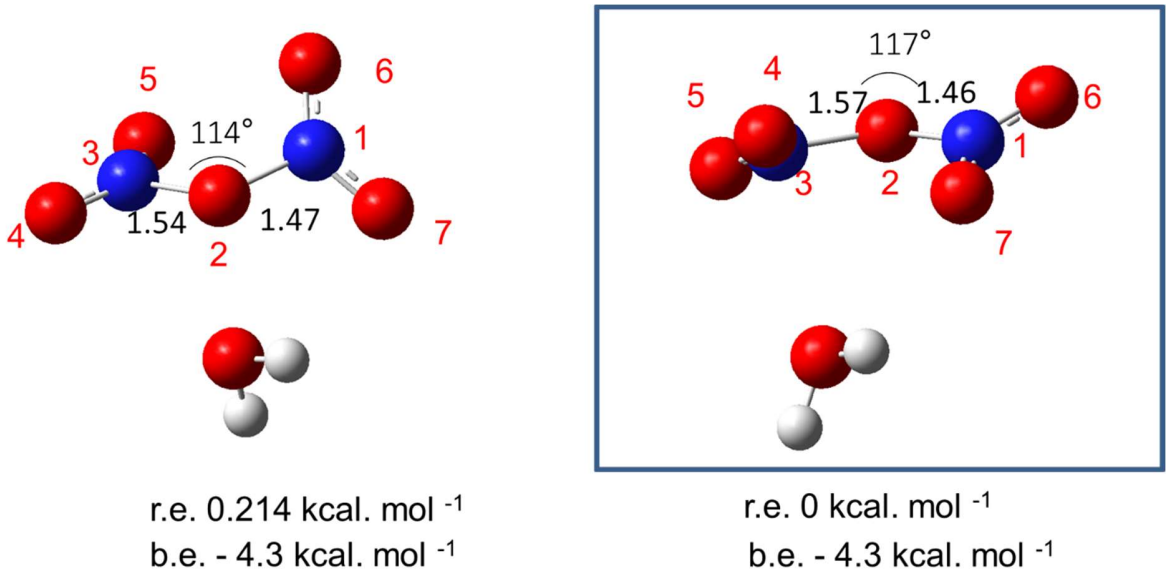
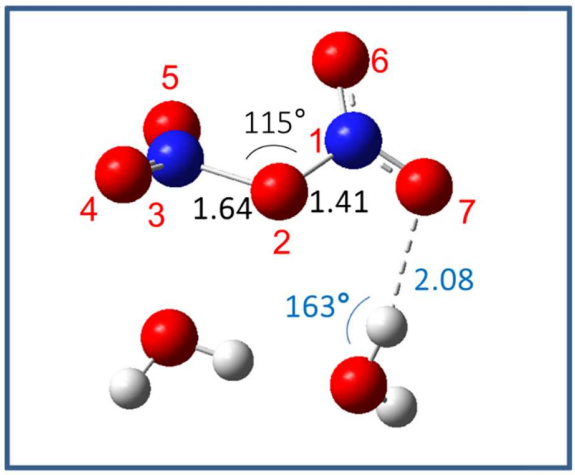


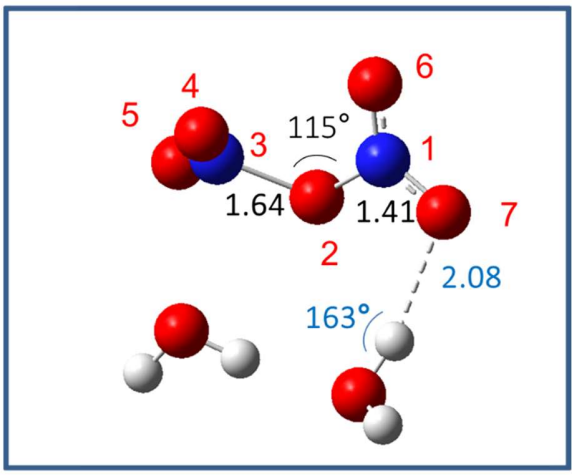
Figure S1. Optimized structures for the C_2 and Cs isomers of N_2O_5 at the ωB97X-D/aug-cc-pVTZ level of theory. The experimental values by McClleland et al.[1,2] are shown in green for the C_2 isomer.





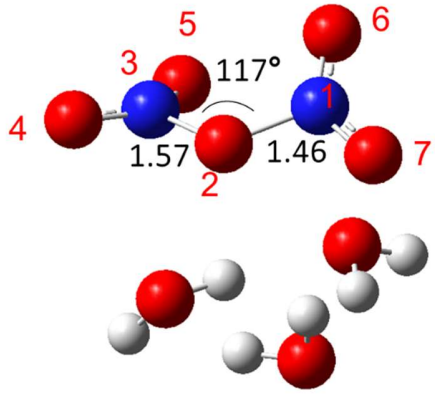
r.e. 0.005 kcal. mol $^{-1}$
b.e. – 8.78 kcal. mol $^{-1}$

(c)



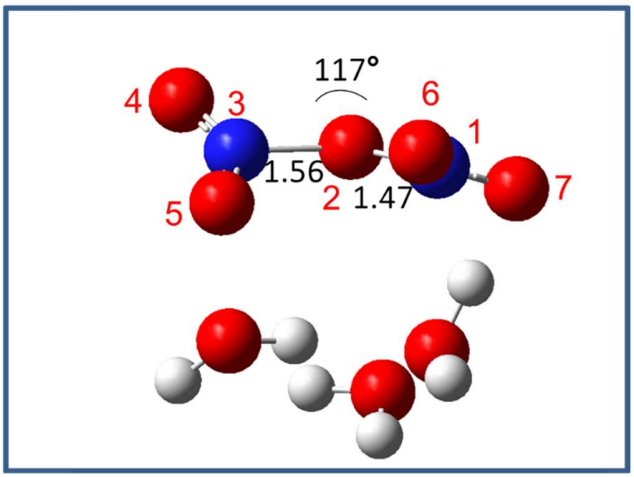
r.e. 0 kcal. mol $^{-1}$
b.e. – 8.78 kcal. mol $^{-1}$

(d)



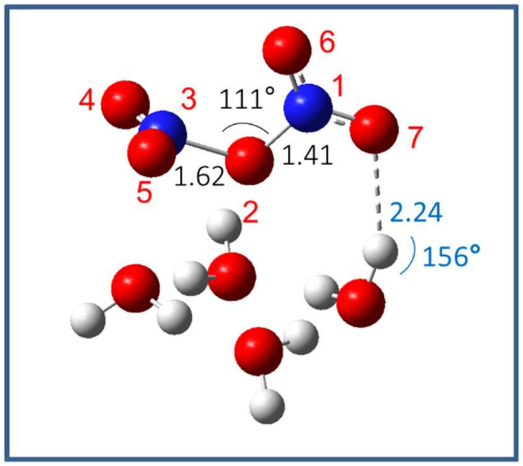
r.e. 0.59 kcal. mol $^{-1}$
b.e. – 6.99 kcal. mol $^{-1}$

(e)



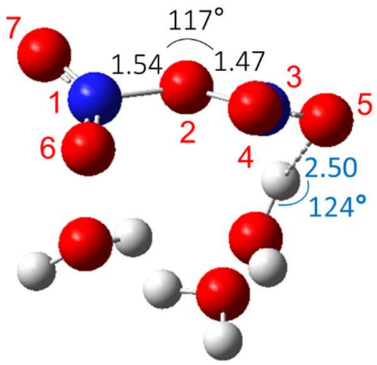
r.e. 0 kcal. mol $^{-1}$
b.e. – 7.14 kcal. mol $^{-1}$

(f)



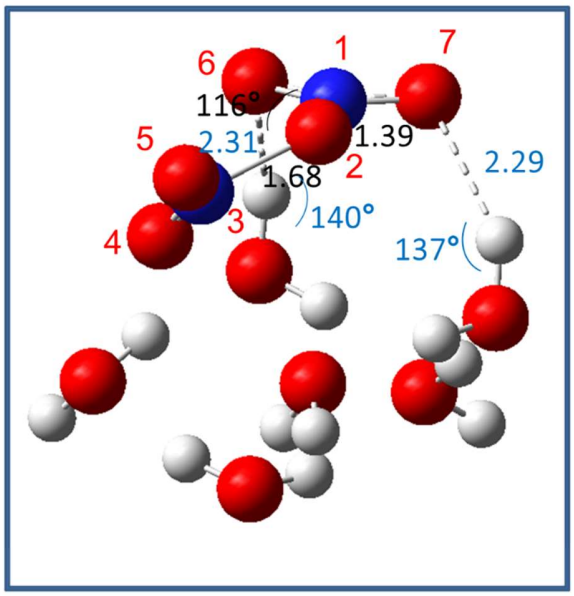
r.e. 0 kcal. mol $^{-1}$
b.e. –7.59 kcal. mol $^{-1}$

(g)



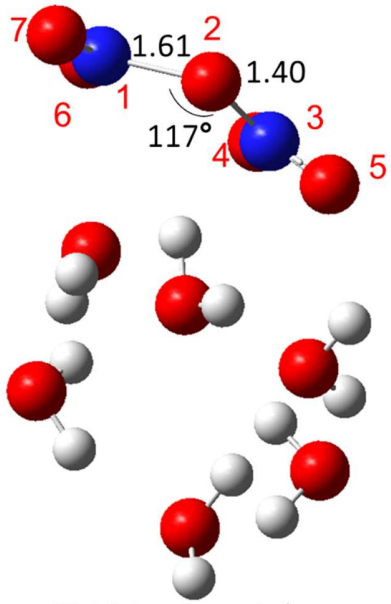
r.e. 4.87 kcal. mol $^{-1}$
b.e. – 7.68 kcal. mol $^{-1}$

(h)



r.e. 0 kcal. mol $^{-1}$
b.e. –10.36 kcal. mol $^{-1}$

(i)



r.e. 7.43 kcal. mol $^{-1}$
b.e. – 12.80 kcal. mol $^{-1}$

(j)

Figure S2. $N_2O_5 \cdot (H_2O)_n$ structures for: (a) and (b), n = 1; (c) and (d), n = 2; (e) and (f), n = 3; (g) and (h), n = 4 and (i) and (j), n = 6.

Table TS1. Partial charge on $NO_2^{\delta+}$ for $N_2O_5 \cdot (H_2O)_n$ clusters with n = 1, 2, 3, 4, 6, 10, 15, 20. "(e)" marks encapsulated structures while "(s)" marks surface structures. The data is grouped according to initial C_2 or Cs N_2O_5 structure.

n	C_2	C_s
1	**0.14**	**0.23**
2	**0.31**	**0.31**
3	**0.13**	**0.22**
4	**0.28**	**0.21**
6	**0.35**	**0.30**
10	**0.46**	**0.20**
15	**0.32**	**0.26**
20(s)	**0.37**	**0.36**
20(e)	**0.59**	**0.35**

Table TS2. QTAIM analysis of hydrogen bonds for $N_2O_5 \cdot (H_2O)_n$ clusters with n = 10-20. The hydrogen bond energies are estimated using the de Espinosa method. "(e)" marks encapsulated structures while "(s)" marks surface structures. The data is grouped according to initial C_2 or Cs N_2O_5 structure. Bonds in green are in agreement with the geometrical criteria used in the main text. Bonds in red appear in the QTAIM analysis but not in the analysis based on geometric criteria.

n	initial symmetry	# of H-bonds	V [a.u.]	0.5*|V| [kcal mol^{-1}]
10	C_2	BCP H9 O2	-9.45E-03	2.96
		BCP O6 H12	-8.13E-03	2.55
		BCP H30 O7	-1.23E-02	3.86
10	C_s	BCP O7 H13	-8.18E-03	2.57
15	C_2	BCP O6 H12	-5.99E-03	1.88
		BCP H30 O7	-1.04E-02	3.26
15	C_s	BCP H26 O22	-8.57E-03	2.69
20(s)	C_2	BCP O6 H36	-5.42E-03	1.70
		BCP O7 H10	-1.22E-02	3.83
20(e)	C_2	BCP O6 H27	-1.49E-02	4.68
		BCP H31 O7	-6.84E-03	2.15
		BCP H43 O7	-1.49E-02	4.69
20(s)	C_s	BCP H15 O4	-1.60E-02	5.02

		BCP H57 O5	-1.08E-02	3.39
20(e)	C_s	BCP H9 O2	-9.74E-03	3.06
		BCP H54 O2	-3.59E-03	1.13
		BCP H37 O5	-1.39E-02	4.36

References

1 B. M. McClelland, A. D. Richardson and K. Hedberg, *Helv. Chim. Acta*, 2001, **84**, 1612–1624.

2 B. W. McClelland, L. Hedberg, K. Hedberg and K. Hagen, *J. Am. Chem. Soc.*, 1983, **105**, 3789–3793.

3 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.

4 R. F. W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9–15.

5 E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170–173.

6 T. A. Keith, 2017, TK Gristmill Software, Overland Park KS, USA.