Supplementary Information for

Complexes of HNO_3 and NO_3^- with NO_2 and N_2O_4, and Their Potential Role in Atmospheric HONO Formation

Michael A. Kamboures[1]
Jonathan D. Raff[1]
Yifat Miller[2]
Leon F. Phillips[3]
Barbara J. Finlayson-Pitts[1]
R. Benny Gerber[1,2]*

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1. Department of Chemistry, University of California, Irvine, CA 92697
   USA
2. Department of Physical Chemistry and the Fritz Haber Research Center for Molecular Dynamics, Hebrew University, Jerusalem 91904, Israel
3. Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

* Author to whom correspondence should be addressed. Telephone: 972-2-651-5732; FAX: 972-2-651-3742; e-mail: bgerber@uci.edu

Table S1 Vibrational frequencies, infrared intensities, and Raman intensities for HNO_3 obtained using ROMP2/TZP

HNO_3		Frequencies		Calculate Intensities	
Mode	Description	Calculated (cm^{-1})	Experimental (cm^{-1})	Infrared ($km \cdot mol^{-1}$)	Raman ($Å^4 \cdot amu^{-1}$)
1	OH stretch	3784	3492 [a]	91	43
2	asymmetric stretch	1864	1698 [a]	270	13
3	HON bend	1351	1346 [a]	120	5.4
4	ONO symmetric stretch	1314	1312 [a]	210	22
5	(H)ON stretch	895	903 [a]	230	8.4
6	OOON torsion	760	768 [a]	6	0.1
7	ONO bend	661	664 [a]	25	9.5
8	(H)ONO bend	592	598 [a]	9	4.2
9	HONO torsion	459	479 [a]	150	1.6

[a] W. A. Guillory and M. L. Bernstein, *J. Chem. Phys.*, 1975, **62**, 1058-1060.

Table S2 Vibrational frequencies, infrared intensities, and Raman intensities for NO_2 obtained using ROMP2/TZP

NO_2		Frequencies		Calculated Intensities	
Mode	Description	Calculated (cm^{-1})	Experimental (cm^{-1})	Infrared ($km \cdot mol^{-1}$)	Raman ($Å^4 \cdot amu^{-1}$)
1	Asymmetric Stretch	1844	1618 [a]	220	39
2	ONO Symmetric Stretch	1322	1318 [a]	6.9	77
3	Bend	773	750 [a]	4.3	2.2

[a] T. Schimanouchi, *Tables of Molecular Vibrational Frequencies. Part 5.*, NSRDS-NBS 39, 1972.

Table S3 Vibrational frequencies, infrared intensities, and Raman intensities for N_2O_4 obtained using ROMP2/TZP

N_2O_4		Frequencies		Calculated Intensities	
Mode	Description	Calculated (cm^{-1})	Experimental (cm^{-1})	Infrared ($km \cdot mol^{-1}$)	Raman ($Å^4 \cdot amu^{-1}$)
1	in phase ONO asymmetric stretch	1947	1761 [a]	310	0.0
2	180° out of phase ONO asymmetric stretch	1917	1718 [b]	0.0	22
3	in phase ONO symmetric stretch	1405	1383 [b]	0.0	11
4	180° out of phase symmetric stretch	1270	1261 [a]	430	0.0
5	in phase ONO bend	829	813 [c]	0.0	10
6	180° out of phase ONO bend	750	751 [a]	270	0.0
7	NOON torsion	637	657 [b]	0.0	0.81
8	in phase ONN bend	470	480 [d]	0.0	8.3
9	OOON torsion	400	425 [d]	8.3	0.0
10	NN stretch	257	262 [c]	0	44
11	180 ° out of phase ONN bend	202	265 [e]	0.12	0.13
12	ONNO torsion	92	82 [d]	0.0	0.0

[a] E. L. Varetti and G. C. Pimentel, *J. Chem. Phys.*, 1971, **55**, 3813.
[b] F. Bolduan and H. J. Jodl, *Chem. Phys. Lett.*, 1982, **85**, 283-286.
[c] D. E. Tevault and L. Andrews, *Spectrochim. Acta*, 1974, **30A**, 969.
[d] C. H. Bibart and G. E. Ewing, *J. Chem. Phys.*, 1974, **61**, 1284-1292.
[e] D. Luckhaus and M. Quack, *Chem. Phys. Lett.*, 1992, **199**, 293-301.

Table S4 Vibrational frequencies, infrared intensities, and Raman intensities for NO_3^- obtained using ROMP2/TZP

NO_3^-		Frequencies		Calculated Intensities	
Mode	Description	Calculated (cm^{-1})	Experimental (cm^{-1})	Infrared ($km \cdot mol^{-1}$)	Raman ($Å^4 \cdot amu^{-1}$)
1	Asymmetric stretch	1493	1356 [a]	620	8.5
2	Asymmetric stretch	1493	1356 [a]	620	8.6
3	Symmetric stretch	1066	1050[b]	0	45
4	OOON torsion	833	831[b]	11	0.0
5	ONO bend	726	720[b]	0.59	5.6
6	ONO bend	726	720[b]	0.59	5.7

[a] D. Forney, W. E. Thompson and M. E. Jacox, *J. Chem. Phys.*, 1993, **99**, 7393.
[b] G. Herzberg, *Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, New Jersey, 1945, p. 178.

Additional configurations of (HONO)·(NO_3).

Two other stable configurations of (HONO)·(NO_3) were located in addition to the one shown in Fig 4. The first of these is displayed in Fig. S1. This configuration appears to be the global minimum energy structure for (HONO)·(NO_3) and contains HONO in the *trans* conformation. The second structure has a slightly potential energy and is shown in Fig. 6b. The potential energies of these structures are 42.1 kcal·mol^{-1} and 43.1 kcal·mol^{-1} greater than combined energy of isolated HNO_3 and NO_2. The potential energy of the *trans* complex is 3.5 kcal·mol^{-1} less than the combined energies of isolated NO_3 and HONO. After ZPE is taken into consideration, the ROMP2 binding energy of the global minimum (*trans*-HONO)·(NO_3) is -3.3 kcal·mol^{-1}.

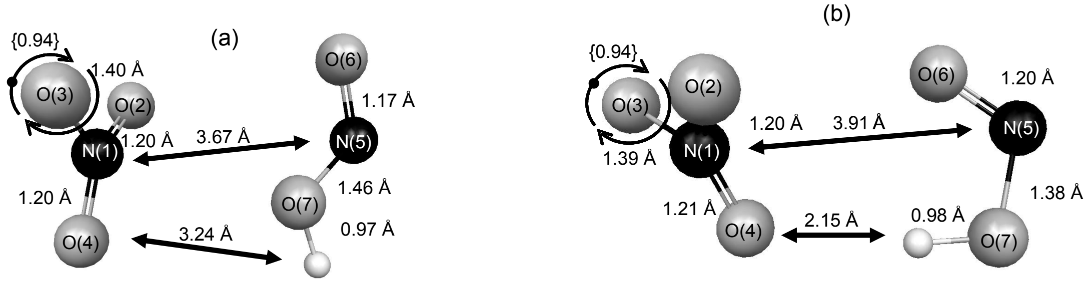

Fig. S1 Structural isomers of (HONO)·(NO_3): (a) global minimum structure, and (b) local minimum structure.