10.1071/CH17581_AC

Australian Journal of Chemistry 2018, 71(4), 265-271

Supplementary Material

Anion photoelectron spectroscopy and high level ab initio calculations of the halide-nitric oxide dimer complexes

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Table S1: *Structural parameters and energies of bare nitric oxide molecule, bare halide anions, and bare halogen radicals predicted from MP2 calculations*

		r_{N-O}	$E_{CCSD(T)}$	zpe	VDE	Exp. SO ∗	Split	Literature $^2P_{3/2}$ VDE †	Shift ‡
		Å	E_h	kJ mol^{-1}	eV	eV	eV	eV	eV
N=O	apvtz	1.153	-129.726116	12.6					
	apvtz//qz		-129.758086						
	apvtz//5z		-129.768338						
	CBS		-129.761389						
Cl^- | Cl	apvtz		-459.806626 | -459.677858		3.504	-0.036 | +0.073	3.468 | 3.577	3.613	+0.145
	apvqz		-459.828395 | -459.695891		3.606		3.570 | 3.679		+0.043
	apv5z		-459.834835 | -459.701313		3.633		3.597 | 3.706		+0.016
	CBS		-459.841344 | -459.706710		3.664		3.627 | 3.737		-0.014
Br^- | Br	apvtz		-415.836425 | -415.713279		3.351	-0.152 | +0.305	3.199 | 3.656	3.364	+0.165
	apvqz		-415.912356 | -415.785328		3.457		3.305 | 3.762		+0.059
	apv5z		-415.991187 | -415.863015		3.488		3.336 | 3.793		+0.028
	CBS		-416.073854 | -415.944439		3.522		3.369 | 3.826		-0.005
I^- | I	apvtz		-294.982288 | -294.865413		3.180	-0.315 | +0.628	2.865 | 3.808	3.059	+0.194
	apvqz		-295.061242 | -294.939975		3.300		2.985 | 3.928		+0.074
	apv5z		-295.116483 | -294.993899		3.336		3.020 | 3.964		+0.039
	CBS		-295.174430 | -295.050402		3.374		3.061 | 4.003		-0.002

∗ Values from http://www.nist.gov/pml/data/handbook/index.cfm

† Values from http://webbook.nist.gov

‡ Shift refers to the difference between the predicted and literature Electron Detachment Energy

Table S2: *Structural parameters of the C_s halide-nitric oxide gas phase van der Waals **anion** complexes predicted from CCSD(T) calculations*

	$r_{X\cdots N}$	r_{N-O}	$\angle_{(X-N-O)}$	zpe	$E_{CCSD(T),anion}$	$E_{CCSD(T),radical}$ *	D_e	D_0 †	VDE ‡
	Å	Å	°	kJ mol^{-1}	E_h	E_h	kJ mol^{-1}	kJ mol^{-1}	eV
$Cl^-\cdots NO$									
apvtz	2.982	1.159	102.6	13.7	-589.531675	-589.413721	16.4	15.3	3.510 | 3.619
apvtz//qz					-589.592730	-589.463445			
apvtz//5z					-589.609418	-589.479061			
CBS					-589.625632	-589.494160			
$Br^-\cdots NO$									
apvtz	3.149	1.159	103.7	13.6	-545.568181	-545.447551	14.3	13.3	3.322 | 3.778
apvtz//qz					-545.676157	-545.550822			
apvtz//5z					-545.765112	-545.638273			
CBS					-545.857337	-545.728929			
$I^-\cdots NO$									
apvtz	3.464	1.158	103.7	13.3	-424.712943	-424.597380	12.4	11.7	3.093 | 4.036
apvtz//qz					-424.823932	-424.702287			
apvtz//5z					-424.889480	-424.765866			
CBS					-424.957185	-424.831504			

∗ CCSD(T) single point energy calculation for radical species (Charge 0, Multiplicty 1) at anion geometry

† Calculated using CCSD(T)/CBS energy and CCSD(T)/aug-cc-pVTZ zpe, along with data in S1

‡ Vertical Detachment energy: CCSD(T)/CBS of neutral at anion geometry, inclusive of CCSD(T)/aug-cc-pVTZ zpe, shifted and split into $^2P_{3/2}$ and $^2P_{1/2}$ components using data in Table S1

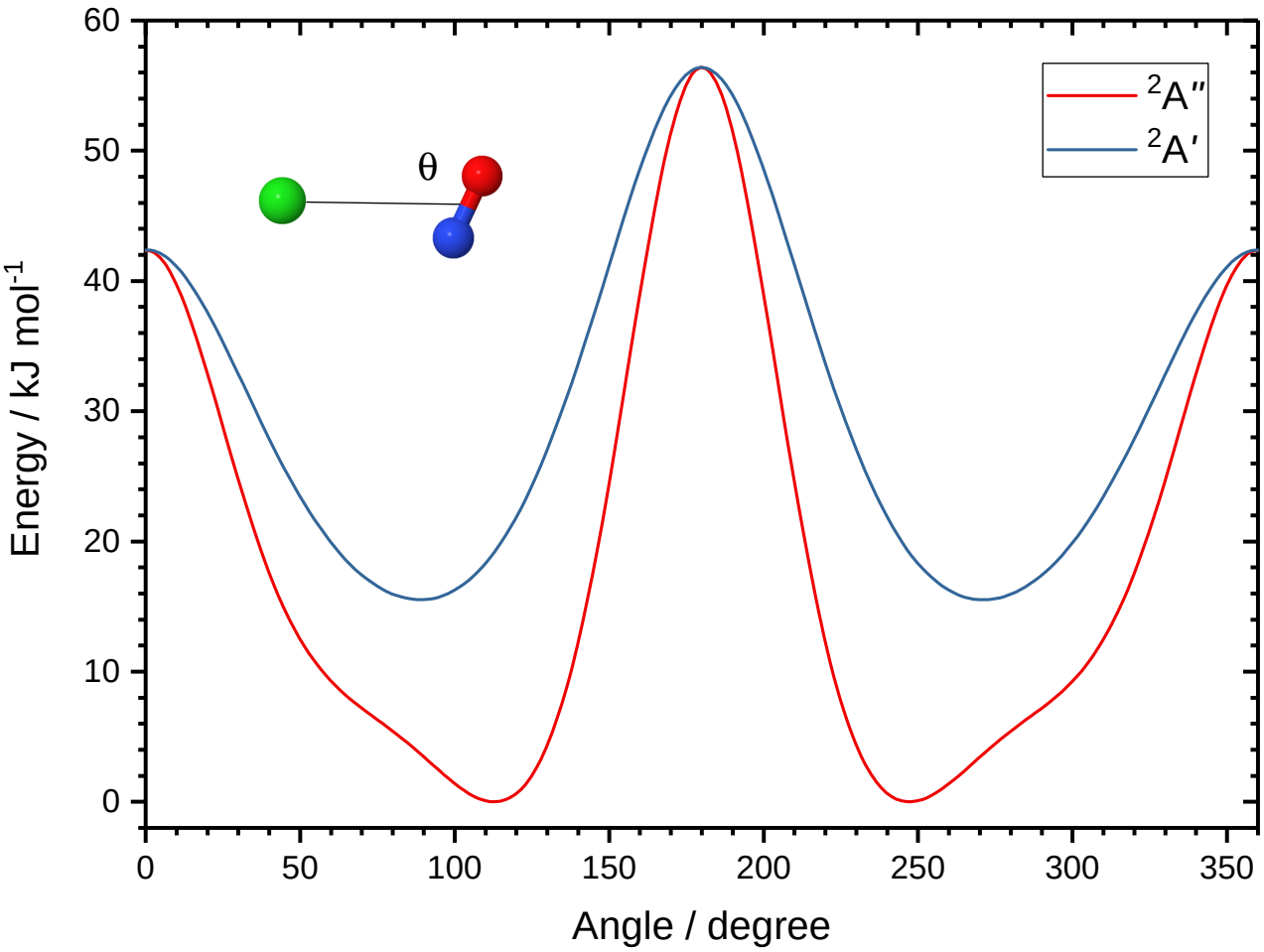

Figure S1: *Potential energy curves corresponding to internal rotation of the NO molecule in the $Cl^{-}\cdots NO$ complex in the $^{2}A''$ and $^{2}A'$ states. θ is defined on the Figure.*

Table S3: *Predicted vibrational frequencies for the C_S halide-nitric oxide **anion** complexes, and bare nitric oxide, from CCSD(T) calculations. Calculations employ aug-cc-pVTZ basis sets (aug-cc-pV(T+d)Z for Cl, and PP variants for Br and I). Frequencies in* cm^{-1}. *Also provided are zero point energies (zpe) in* $\mathrm{kJ\,mol}^{-1}$, *mode symmetries, and approximate descriptions.*

	Symmetry	$Cl^-\cdots NO$	$Br^-\cdots NO$	$I^-\cdots NO$	N=O	Mode Description
ω_1	a' (σ_g^+)	2020	2035	2060	2112	N=O stretch
ω_2	a'	181	159	112		X···N stretch
ω_3	a'	99	84	59		X···N=O bend
zpe		13.8	13.6	13.3	12.6	

Table S4: *Cartesian coordinates describing the geometries of halide-nitric oxide complexes, and bare nitric oxide, optimised at CCSD(T)/apvtz, in* Å.

		x	y	z
	Cl	-1.46560298	0.03449458	0.00000000
$Cl^-\cdots NO$	N	1.44855753	-0.60112825	0.00000000
	O	1.93600260	0.45085627	0.00000000
	Br	-0.92223020	0.01449716	0.00000000
$Br^-\cdots NO$	N	2.16596966	-0.59870021	0.00000000
	O	2.65400853	0.45261585	0.00000000
	I	-0.69975095	0.00796015	0.00000000
$I^-\cdots NO$	N	2.71092336	-0.59832377	0.00000000
	O	3.17852683	0.46065846	0.00000000
	N	0.00000000	0.00000000	0.61487489
N=O	O	0.00000000	0.00000000	-0.53830475