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Supplementary Material

The bromide-carbon monoxide gas phase complex: Anion photoelectron spectroscopy and *ab initio* calculations

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Calculated data for anion and neutral Br…CO complexes

Calculations were performed at the MP2, CCSD, and CCSD(T) levels of theory, employing Dunning's correlation consistent basis sets aug-cc-pvxz (x=d,t,q) for carbon and oxygen,(1-3) and the aug-cc-pvxz PP basis sets with ECPs for bromine (x = d,t,q).(4)

Bond lengths are denoted *r*(A-B), and are given in Ångström (10^{-10} metre)

Angles are denoted by θ(A-B-C), and are given in degrees

Zero point energy (zpe), given in $kJ.mol^{-1}$

E_e and $E_{e/BSSE}$ are the electronic energies, and those corrected for Basis Set Superposition Error (BSSE), in units of hartrees.

D_o and D_e are calculated using BSSE corrected energies, and are given in $kJ.mol^{-1}$

Vibrational data given in units of cm^{-1}, while the infrared intensities are in km/mol (bold text following the vibrational wavenumber)

Also provided are calculated adiabatic photodetachment energies, from the anion to the neutral complexes.

(1) T H Dunning, J. Chem. Phys. 90 (1989) 1007-23.
(2) R A Kendall, T H Dunning, R J Harrison, J. Chem. Phys. 96 (1992) 6796-806.
(3) D E Woon, T H Dunning, J. Chem. Phys. 98 (1993) 1358-71.
(4) K A Peterson, D Figgen, E Goll, H Stoll, M Dolg, Journal of Chemical Physics 119 (2003) 11113-23.

	MP2			***CCSD***		***CCSD(T)***	
	pvdz	***pvtz***	***pvqz***	***pvdz***	***pvtz***	***pvdz***	***pvtz***
***r*(C≡O) /Å**	1.150	1.139	1.135	1.141	1.129	1.147	1.136
***ω₁ (σ) /cm*$^{-1}$**	2072 **34**	2110 **36**	2123 **37**	2172 **75**	2215 **77**	2105	2145
zpe /kJ.mol^{-1}	12.4	12.6	12.7	13.0	13.3	12.6	12.8
E$_e$ /hartree	-113.054970	-113.142411	-113.172923	-113.061313	-113.144520	-113.074053	-113.162194

Carbon Monoxide, CO

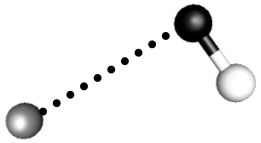
Bare Anion & Neutral

		MP2					
		pvdz	***pvtz***	***pvqz***	***pvdzPP***	***pvtzPP***	***pvqzPP***
E$_e$ /hartree	Br$^-$	-2572.609288	-2572.774831	-2572.849758	-415.723399	-415.858439	-415.975342
	Br	-2572.484321	-2572.646685	-2572.718075	-415.599802	-415.731957	-415.845433

		CCSD		***CCSD(T)***	
		pvdzPP	***pvtzPP***	***pvdzPP***	***pvtzPP***
E$_e$ /hartree	Br$^-$	-415.730761	-415.863137	-415.735061	-415.874434
	Br	-415.612120	-415.743089	-415.614837	-415.751404

Anion…CO Complexes

Br^- …CO, C_s symmetry minimum.



	r(Br…C) /Å	*r(C-O) /Å*	*θ(Br-C-O)) / °*	*zpe /kj.mol^{-1}*	*E_e /hartree*	*$E_{e/BSSE}$ /hartree*	*D_e /kj.mol^{-1}*	*D_o /kj.mol^{-1}*
MP2/pvdz	3.444	1.152	94.5	13.4	-2685.668869	-2685.667686	9.0	8.0
MP2/pvtz	3.383	1.141	94.5	13.6	-2685.922132	-2685.921254	10.5	9.5
MP2/pvqz	3.366	1.137	94.4	13.8	-2686.027687	-2686.026969	11.3	10.2
MP2/pvdzPP	3.413	1.152	95.1	13.4	-528.783192	-528.781763	8.9	7.9
MP2/pvtzPP	3.319	1.141	95.7	13.7	-529.006223	-529.004837	10.5	9.4
MP2/pvqzPP	3.270	1.138	96.2	13.9	-529.153934	-529.152473	11.1	9.9
CCSD/pvdzPP	3.444	1.143	98.2	14.0	-528.796674	-528.795356	8.6	7.6
CCSD/pvtzPP	3.393	1.132	97.9	14.3	-529.012570	-529.011411	9.9	8.8
CCSD(T)/pvdzPP	3.371	1.151	98.9	13.7	-528.814228	-528.812622	9.2	8.1
CCSD(T)/pvtzPP	3.303	1.140	98.8	13.9	-529.042113	-529.040777	10.9	9.9

Vibrational Data, in units of cm^{-1}

	MP2			***MP2***			***CCSD***		***CCSD(T)***	
	pvdz	***pvtz***	***pvqz***	***pvdzPP***	***pvtzPP***	***pvqzPP***	***pvdzPP***	***pvtzPP***	***pvdzPP***	***pvtzPP***
ω_1 a´	2059 **44**	2094 **47**	2107 **47**	2057 **46**	2090 **52**	2101 **55**	2149 **89**	2190 **91**	2077	2114
ω_2 a´	119 **1**	121 **1**	124 **1**	122 **1**	128 **2**	136 **2**	132 **2**	134 **2**	137	139
ω_3 a´	67 **6**	66 **7**	70 **7**	69 **6**	69 **7**	77 **7**	66 **6**	64 **6**	71	70

Neutral…CO Complexes

Br…CO, $C_{\infty v}$ symmetry minimum

	r(Br…C) /Å	*r(C-O) /Å*	*θ(Br-C-O)) / °*	*zpe /kj.mol^{-1}*	*E_e /hartree*	*$E_{e/BSSE}$ /hartree*	*D_e /kj.mol^{-1}*	*D_o /kj.mol^{-1}*
MP2/pvdz	3.128	1.149	180.0	13.4	-2685.542617	-2685.540866	4.1	3.1
MP2/pvtz	2.979	1.138	180.0	13.7	-2685.792748	-2685.791071	5.2	4.1
MP2/pvqz	2.992	1.134	180.0	13.7	-2685.894588	-2685.893485	6.5	5.5
MP2/pvdzPP	3.077	1.149	180.0	13.5	-528.658616	-528.656379	4.2	3.1
MP2/pvtzPP	2.890	1.137	180.0	13.8	-528.878979	-528.876270	5.0	3.8
MP2/pvqzPP	2.896	1.134	180.0	13.7	-529.023352	-529.020824	6.5	5.4
CCSD/pvdzPP	3.155	1.139	180.0	14.1	-528.676658	-528.674603	3.1	2.0
CCSD/pvtzPP	3.040	1.127	180.0	14.4	-528.891036	-528.888914	3.4	2.3
CCSD(T)/pvdzPP	3.063	1.146	180.0	13.6	-528.692716	-528.690302	3.7	2.7
CCSD(T)/pvtzPP	2.911	1.134	180.0	13.9	-528.917902	-528.915345	4.6	3.5

Vibrational Data, in units of cm^{-1}

	MP2			***MP2***			***CCSD***		***CCSD(T)***	
	pvdz	***pvtz***	***pvqz***	***pvdzPP***	***pvtzPP***	***pvqzPP***	***pvdzPP***	***pvtzPP***	***pvdzPP***	***pvtzPP***
ω_1 σ^+	2082 **35**	2120 **36**	2132 **36**	2083 **35**	2122 **36**	2134 **37**	2183 **81**	2228 **83**	2117	2158
ω_2 σ^+	65 **1**	69 **2**	62 **2**	68 **1**	78 **2**	70 **2**	65 **1**	67 **1**	70	77
ω_3 π	47 **<1**	53 **<1**	46 **<1**	49 **<1**	53 **<1**	47 **<1**	50 **<1**	59 **<1**	48	45

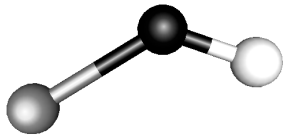
Br…OC linear structure, $C_{\infty v}$ symmetry minimum

	r(Br…O) /Å	***r(C-O) /Å***	***θ(Br-O-C)) / °***	***zpe /kj.mol^{-1}***	***E_e /hartree***	***$E_{e/BSSE}$ /hartree***	***D_e /kj.mol^{-1}***	***D_o /kj.mol^{-1}***
MP2/pvdz	3.282	1.151	180.0	13.0	-2685.540929	-2685.539975	1.8	1.2
MP2/pvtz	3.214	1.139	180.0	13.3	-2685.790848	-2685.789932	2.2	1.5
MP2/pvqz	3.212	1.136	180.0	13.3	-2685.892695	-2685.891976	2.6	1.9
MP2/pvdzPP	3.232	1.151	180.0	13.1	-528.656680	-528.655394	1.6	1.0
MP2/pvtzPP	3.150	1.140	180.0	13.4	-528.876615	-528.875160	2.1	1.3
MP2/pvqzPP	3.091	1.136	180.0	13.5	-529.020859	-529.019178	2.2	1.4
CCSD/pvdzPP	3.288	1.141	180.0	13.6	-528.675166	-528.673986	1.5	0.8
CCSD/pvtzPP	3.223	1.129	180.0	14.0	-528.889522	-528.888266	1.7	1.0
CCSD(T)/pvdzPP	3.239	1.147	180.0	13.2	-528.690812	-528.689507	1.6	1.0
CCSD(T)/pvtzPP	3.179	1.137	180.0	13.4	-528.915763	-528.914408	2.1	1.5

Vibrational Data, in units of cm^{-1}

	MP2			***MP2***			***CCSD***		***CCSD(T)***	
	pvdz	***pvtz***	***pvqz***	***pvdzPP***	***pvtzPP***	***pvqzPP***	***pvdzPP***	***pvtzPP***	***pvdzPP***	***pvtzPP***
ω_1 σ^+	2082 **35**	2120 **36**	2132 **36**	2070 **46**	2106 **49**	2119 **51**	2169 **95**	2211 **99**	2101	2141
ω_2 σ^+	65 **1**	69 **2**	62 **2**	53 <1	60 <**1**	67 <**1**	49 <**1**	55 <**1**	53	58
ω_3 π	47 <**1**	53 <**1**	46 <**1**	30 **1**	35 **1**	32 <**1**	32 <**1**	38 <**1**	26	24

BrCO, C_s symmetry minimum



	r(Br-C) /Å	***r(C-O) /Å***	***θ(Br-C-))) / ^{o}***	***zpe /kj.mol^{-1}***	***E_e /hartree***	***$^*\Delta E$ / kJ.mol^{-1}***
MP2/pvdz	2.067	1.164	130.6	15.2	-2685.536377	18.2
MP2/pvtz	2.001	1.158	130.1	16.1	-2685.791672	5.2
MP2/pvqz	1.980	1.156	130.0	16.4	-2685.895844	-0.6
MP2/pvdzPP	2.054	1.164	130.7	15.3	-528.653206	16.0
MP2/pvtzPP	1.993	1.158	130.3	16.1	-528.878909	2.5
MP2/pvqzPP	1.963	1.157	130.3	16.5	-529.026900	-6.5
CCSD/pvdzPP	Converged to Br…CO					
CCSD/pvtzPP						
CCSD(T)/pvdzPP	Converged to Br…CO					
CCSD(T)/pvtzPP						

* The ΔE values are calculated with respect to the Br…CO complex, using BSSE uncorrected energies

Vibrational Data, in units of cm^{-1}

	MP2			***MP2***		
	pvdz	***pvtz***	***pvqz***	***pvdzPP***	***pvtzPP***	***pvqzPP***
ω_1 a´	1923 **386**	1924 **452**	1931 **467**	1918 **404**	1924 **460**	1929 **482**
ω_2 a´	463 **40**	519 **73**	541 **84**	470 **45**	522 **75**	555 **89**
ω_3 a´	148 **46**	241 **42**	266 **37**	164 **47**	245 **41**	280 **33**

Calculated detachment energies for the Br^- anion to the neutral, in units of eV. E_{Shift} is the adjustment required to bring the calculated energies in line with experiment.

	Barycentre	$^2P_{3/2}$, $^2P_{1/2}$	E_{Shift}
MP2/pvdz	3.401	3.249, 3.706	0.102
MP2/pvtz	3.487	3.335, 3.792	0.016
MP2/pvqz	3.583	3.431, 3.888	-0.080
MP2/pvdz PP	3.363	3.211, 3.668	0.140
MP2/pvtz PP	3.442	3.290, 3.747	0.061
MP2/pvqz PP	3.535	3.383. 3.840	-0.032
CCSD/pvdz PP	3.228	3.076, 3.533	0.275
CCSD/pvtz PP	3.267	3.115, 3.572	0.236
CCSD(T)/pvdz PP	3.272	3.120, 3.577	0.231
CCSD(T)/pvtz PP	3.348	3.196, 3.653	0.155

Calculated adiabatic detachment energies from Br^-…CO to the neutral minima, in units of eV. Also included are the $^2P_{3/2}$, $^2P_{1/2}$ energies which are produced by splitting the barycentre energy by the experimental Spin orbit splitting, and applying the E_{shift} from the table above. E_{Shift} is the energy shift required to bring the photodetachment energy of the bare anion in line with experiment.

	Br…CO		Br…OC	
	Barycentre	$^2P_{3/2}$, $^2P_{1/2}$	Barycentre	$^2P_{3/2}$, $^2P_{1/2}$
MP2/pvdz	3.451	3.401, 3.858	3.471	3.421, 3.878
MP2/pvtz	3.543	3.407, 3.864	3.570	3.434, 3.891
MP2/pvqz	3.631	3.399, 3.856	3.668	3.436, 3.893
MP2/pvdz PP	3.413	3.401, 3.858	3.436	3.424, 3.881
MP2/pvtzPP	3.500	3.409, 3.866	3.526	3.435, 3.892
MP2/pvqz PP	3.580	3.396, 3.853	3.623	3.439, 3.896
CCSD/pvdz PP	3.287	3.41, 3.867	3.299	3.422, 3.879
CCSD/pvtz PP	3.334	3.418, 3.875	3.348	3.432, 3.889
CCSD(T)/pvdz PP	3.328	3.407, 3.864	3.345	3.424, 3.881
CCSD(T)/pvtz PP	3.413	3.416, 3.873	3.434	3.437, 3.894