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Supporting Information

Flexible Bonding Between Copper and Nitric Oxide: Infrared Photodissociation Spectroscopy of Copper Nitrosyl Cation Complexes: $[Cu(NO)_n]^+$ (n=1-5)

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Table S1. Vibrational frequencies (cm^{-1}, scaled), total energy (Hartree) and IR intensities (km/mol) for various $[Cu(NO)_n]^+$ and $[Cu(NO)_nAr_m]^+$.

complex	state/symmetry	total energy	vibrational frequencies (IR intensities)
$[Cu(NO)]^+$	$^2A'$, C_s	-326.901158	211(2), 334(7), 1910(278)
$[Cu(NO)Ar]^+$		-854.407635	58(0), 66(1), 195(4), 224(11), 371(3), 1916(190)
$[Cu(NO)Ar_2]^+$		-1381.900012	27(2), 55(1), 60(1), 97(3), 135(11), 157(10), 198(3), 350(4), 1905(212)
$[Cu(NO)_2]^+$	^1A, C_2	-456.767348	46(0), 83(0), 98(0), 200(0), 208(1), 290(0), 369(13), 1913(496), 1934(2)
	^3B, C_2	-456.767070	56(0), 71(0), 136(0), 177(1), 187(1), 285(0), 385(11), 191(549), 1940(0)
	$^1A_1$, C_{2v}	-456.756652	98(0), 129(1), 166(0), 218(8), 240(0), 370(0), 405(21), 182(687), 1902(235)
	$^1A'$, C_s	-456.746810	106(4), 131(1), 229(9), 287(9), 289(1), 431(39), 644(2), 1718(211), 1976 (866)
$[Cu(NO)_2Ar]^+$	^1A, C_s	-984.257890	31(0), 37(0), 53(1), 73(0), 101(9), 134(6), 201(0), 214(1), 291(1), 342(12), 1898(538), 1924(34)
	^3B, C_2	-984.256926	38(4), 38(0), 48(0), 72(7), 82(0), 123(5), 175(1), 213(0), 283(0), 363(14), 1892(632), 1928(18)
	$^1A_1$, C_{2v}	-984.255785	23(0), 36(0), 118(0), 133(0),

			159(12), 177(0), 209(5), 243(1), 388(0), 409(14), 1800(676), 1905(206)
	^{1}A, C_s	-984.250780	46(0), 51(0), 115(7), 141(0), 185(6), 268(3), 305(9), 306(0), 444(28), 667(3), 1716(284), 1964(674)
	^{1}A, C_s	-1511.748028	26(0), 33(0), 40(0), 47(0), 51(1), 69(0), 98(6), 105(6), 125(8), 201(0), 214(2), 292(1), 327(11), 1889(537), 1917(47)
	^{1}A, C_{2v}	-1511.746934	14(0), 26(1), 31(0), 57(1), 108(11), 111(0), 134(1), 140(11), 173(0), 216(5), 240(1), 368(0), 397(13), 1799(613), 1900(193)
$[Cu(NO)_2Ar_2]^+$	^{3}A", C_s	-1511.746892	23(0), 30(0), 32(0,) 42(0), 42(2), 47(1), 53(7), 103(7), 121(5), 188(1), 207(1), 302(1), 337(19), 1889(422), 1912(21)
	^{1}A′, C_s	-1511.739724	-10(2), 18(2), 39(1), 66(2), 108(11), 108(8), 137(0), 149(7), 253(1), 299(8), 307(0), 430(24), 666(5), 1712(302), 1949(658)
	^{2}A, C_1	-586.612375	29(0), 40(0), 114(0), 125(0), 129(1), 173(0), 182(1), 188(2), 228(1), 296(4), 366(0), 389(16), 1814(573), 1899(584), 1923(5)
$[Cu(NO)_3]^+$	^{2}A", C_s	-586.611858	37(0), 41(0), 60(0), 120(0), 131(1), 132(1), 191(0), 211(0), 213(0), 272(0), 288(10), 289(9), 1879(529), 1882(572), 1924(6)
	^{4}A", C_s	-586.610000	45(0), 45(0), 63(0), 119(0), 130(0), 152(2), 187(0), 194(0), 224(2), 289(5), 299(21), 303(18), 1865(708), 1866(697), 1923(1)
	^{2}A, C_1	-1114.101817	24(0), 29(0), 35(0), 49(0), 97(7), 108(2), 120(0), 138(0), 167(1), 195(2), 204(2), 224(1), 292(5), 351(0), 377(14), 1812(524), 1888(618), 1917(20)
$[Cu(NO)_3Ar]^+$	^{2}A", C_s	-1114.101565	35(0), 38(0), 44(0), 48(0), 58(1), 93(6), 109(0), 128(1), 130(1), 199(0), 210(0), 214(1), 278(4), 285(10), 286(5), 1872(514),

			1876(570), 1919(20)
	^4A, C_1	-1114.099300	42(0), 42(0), 52(0), 57(0), 75(1), 94(5), 136(0), 144(1), 144(1), 195(1), 195(1), 206(1), 292(21), 293(22), 296(1), 1855(685), 1855(685), 1916(4)
$[Cu(NO)_4]^+$	$^1A_1$, D_{2d}	-716.454130	30(0), 30(0), 34(0), 105(0), 109(0), 115(0), 132(0), 162(0), 169(0), 184(2), 191(2), 200(0), 225(3), 341(0), 346(0), 347(0), 371(25), 1813(502), 1814(507), 1899(516), 1918(0)
	^3A, C_1	-716.452164	33(0), 44(0), 44(0), 51(0), 108(0), 124(1), 127(0), 131(1), 168(2), 175(0), 201(1), 207(0), 233(3), 274(14), 281(9), 345(3), 357(9), 1811(564), 1852(689), 1866(678), 1919(38)
	D_{2h}	-716.450818	-44(0), 29(0), 62(0), 74(0), 116(0), 119(1), 119(0), 120(0), 131(0), 139(0), 186(3), 195(0), 222(4), 354(0), 363(3), 364(0), 364(0), 1815(0), 1826(910), 1892(691), 1919(0)
$[Cu(NO)_4Ar]^+$	^1A, C_1	-1243.941425	17(0), 31(0), 40(0), 57(1), 65(0), 80(1), 98(1), 112(0), 133(0), 138(0), 161(0), 166(1), 169(0), 201(0), 211(2), 226(3), 337(0), 343(0), 348(0), 370(19), 1812(390), 1818(568), 1896(541), 1917(2)
	C_{2v}	-1243.939727	-3(0), -7(0), 17(0), 21(0), 69(0), 74(0), 87(5), 108(2),115(0), 121(0), 123(0), 128(0), 139(0), 186(4), 195(0), 223(4), 352(0), 360(3), 360(0), 361(0), 1813(0), 1823(879), 1890(672), 1917(2)
	^1A, C_1	-1243.939381	26(0), 28(0), 41(0), 49(1), 59(1), 67(1), 80(0), 87(2), 107(0), 125(0), 132(0), 156(1), 171(1), 182(0), 208(1), 225(3), 262(6), 294(4), 354(4), 359(4), 1808(484), 1861(504), 1877(567), 1915(40)
$[Cu(NO)_5]^+$	^2A, C_1	-846.286770	22(1), 28(0), 32(0), 40(0), 77(0),

			88(4), 102(4), 118(0), 133(0), 136(0), 162(1), 184(1),189(1), 198(2), 238(3), 255(4), 295(8), 304(4), 361(0), 372(28), 411(19), 654(5), 1703(211), 1791(581), 1857(605), 1887(702), 1940(553)
		^{2}A, C_1	-846.285890	25(0), 42(0), 61(0), 65(0), 90(0), 95(0), 103(0), 108(0), 125(0), 133(0), 139(0), 146(0), 154(0), 190(2), 191(1), 196(3), 221(5), 281(0), 319(1), 348(0), 349(4), 359(5), 1803(126), 1816(762), 1835(451), 1884(783), 1916(4)
		^{2}A, C_1	-846.285260	33(0), 38(0), 40(0), 48(0), 63(0), 94(0), 100(0), 121(0), 123(1), 130(0), 139(0), 153(1), 173(0), 185(1), 194(2), 199(4), 233(3), 289(8), 326(14), 343(4), 355(1), 364(1), 1795(227), 1808(740), 1842(584), 1888(825), 1922(17)
		^{2}A, C_1	-846.283374	13(0), 41(0), 45(0), 50(0), 59(0), 77(0), 99(0), 116(1), 122(0), 131(1),136(0), 167(2), 18(1), 190(2), 203(2), 219(1), 235(3), 273(9), 280(10), 323(4), 360(5), 378(5), 1705(308), 1828(986), 1835(623), 1876(564), 1939(478)

Table S2. The Cartesian coordinates (Å) of the optimized structures.

complex	isomer	state/symmetry	Cartesian coordinates			
$[Cu(NO)]^+$		^{2}A', C_s	Cu	0.00000000	0.80371700	0.00000000
			N	0.36497100	-1.06821200	0.00000000
			O	-0.31935000	-1.97878700	0.00000000
$[Cu(NO)Ar]^+$			Cu	0.00000000	0.10657400	0.00000000
			N	0.89997100	1.75453400	0.00000000
			O	1.99434400	2.08131600	0.00000000
			Ar	-1.23636400	-1.77905000	0.00000000
$[Cu(NO)Ar_2]^+$			Cu	0.08645900	0.28829900	0.00000000
			N	0.46575000	2.13030700	0.00000000
			O	-0.13108100	3.10694600	0.00000000
			Ar	-0.13108100	-1.33690000	1.76327800
			Ar	-0.13108100	-1.33690000	-1.76327800
$[Cu(NO)_2]^+$	**a**	^{1}A, C_2	Cu	0.00000000	0.00000000	0.17140700

			N	0.00000000	1.88828200	0.18438000
			O	-0.38246900	2.73998000	-0.47200800
			N	0.00000000	-1.88828200	0.18438000
			O	0.38246900	-2.73998000	-0.47200800
	b	^3B, C_2	Cu	0.00000000	0.00000000	0.08920800
			N	0.00000000	1.87030100	0.16191300
			O	-0.50053200	2.78523100	-0.30336300
			N	0.00000000	-1.87030100	0.16191300
			O	0.50053200	-2.78523100	-0.30336300
	c	$^1A_1$, C_{2v}	Cu	0.00000000	0.00000000	0.96238800
			N	0.00000000	1.51911100	-0.33377800
			N	0.00000000	-1.51911100	-0.33377800
			O	0.00000000	-1.28832700	-1.45227300
			O	0.00000000	1.28832700	-1.45227300
	d	$^1A'$, C_s	Cu	-0.72207300	-1.38382300	0.00000000
			N	1.90753000	1.21644000	0.00000000
			O	1.59018000	2.29086100	0.00000000
			N	0.00000000	0.36762800	0.00000000
			O	-0.64175500	1.33944000	0.00000000
$[Cu(NO)_2Ar]^+$	**a**	^1A, C_s	Cu	0.00000000	0.00000000	0.37517400
			N	0.00000000	1.86096600	0.70145500
			O	-0.63164800	2.66288400	1.21718600
			N	0.00000000	-1.86096600	0.70145500
			O	0.63164800	-2.66288400	1.21718600
			Ar	0.00000000	0.00000000	-2.23196700
	b	^3B, C_2	Cu	0.31571300	-0.08069700	0.00000000
			N	0.75667600	-0.30257300	1.83709800
			O	0.75667600	-1.14044500	2.61483200
			N	0.75667600	-0.30257300	-1.83709800
			O	0.75667600	-1.14044500	-2.61483200
			Ar	-1.76977500	1.37907600	0.00000000
	c	$^1A_1$, C_{2v}	Cu	0.00000000	0.00000000	0.21667000
			N	0.00000000	-1.45547600	-1.15456400
			O	0.00000000	-1.23420900	-2.27635900
			N	0.00000000	1.45547600	-1.15456400
			O	0.00000000	1.23420900	-2.27635900
			Ar	0.00000000	0.00000000	2.57234600
	d	^1A, C_s	Cu	0.00000000	0.66300000	0.00000000
			N	-0.76451200	-2.89159400	0.00000000
			O	0.07543000	-3.63778700	0.00000000
			N	0.37418800	-1.18046700	0.00000000
			O	1.44211900	-1.65028000	0.00000000
			Ar	-0.52267400	2.86566400	0.00000000
$[Cu(NO)_2Ar_2]^+$	**a**	^1A, C_s	Cu	-0.19598900	-0.38258800	0.00000000

			N	-0.66323300	-0.71934600	1.82937900
			O	-0.66323300	-1.61993900	2.53517900
			N	-0.66323300	-0.71934600	-1.82937900
			O	-0.66323300	-1.61993900	-2.53517900
			Ar	-0.83765600	2.25658800	0.00000000
			Ar	2.25880400	0.35924100	0.00000000
	b	^{3}A" C_s	Cu	0.00000000	0.00000000	0.05114600
			N	0.00000000	1.46181100	1.40618700
			O	0.00000000	1.26069000	2.53372000
			N	0.00000000	-1.46181100	1.40618700
			O	0.00000000	-1.26069000	2.53372000
			Ar	-1.76969900	0.00000000	-1.71414900
			Ar	1.76969900	0.00000000	-1.71414900
	c	$^1A_1$, C_{2v}	Cu	-0.53325200	0.31524900	0.00000000
			N	-1.03587200	0.36979600	1.85526000
			O	-1.03587200	-0.40621100	2.69807500
			N	-1.03587200	0.36979600	-1.85526000
			O	-1.03587200	-0.40621100	-2.69807500
			Ar	1.71527700	1.59211900	0.00000000
			Ar	0.87030400	-2.02656200	0.00000000
	d	^{1}A', C_s	Cu	0.02774100	0.31932300	0.00000000
			N	-0.48653300	-3.25318000	0.00000000
			O	0.39037900	-3.96012600	0.00000000
			N	0.54996300	-1.49756000	0.00000000
			O	1.64295600	-1.90627100	0.00000000
			Ar	-0.48653300	1.97016600	1.73654800
			Ar	-0.48653300	1.97016600	-1.73654800
$[Cu(NO)_3]^+$	**a**	^{2}A" C_1	Cu	-0.11425500	-0.17842200	0.00000000
			N	-1.02445600	0.05296700	1.69790300
			O	-1.02445600	0.81058700	2.55563800
			N	1.71644000	-0.82658200	0.00000000
			O	2.75400100	-0.34382600	0.00000000
			N	-1.02445600	0.05296700	-1.69790300
			O	-1.02445600	0.81058700	-2.55563800
	b	^{2}A" C_s	Cu	-0.33038500	-0.12674100	-0.12142500
			N	0.97717800	1.48231400	-0.07463500
			O	2.09456400	1.37547300	0.13392100
			N	1.20424000	-1.37597000	0.01099100
			O	2.30203500	-1.09796300	0.17713300
			N	-2.22890200	-0.05192700	-0.24367900
			O	-3.15740500	0.13431300	0.39801900
	c	^{4}A" C_s	Cu	-0.04351700	0.03371800	0.00000000
			N	1.74356900	0.73834200	0.00000000
			O	2.28163000	1.74922800	0.00000000

			N	-0.97320100	-0.26271800	1.66657100
			O	-0.97320100	-1.02887300	2.51786800
			N	-0.97320100	-0.26271800	-1.66657100
			O	-0.97320100	-1.02887300	-2.51786800
$[Cu(NO)_3Ar]^+$	**a**	^2A, C_1	Cu	-0.17571100	-0.32875400	-0.07607400
			N	1.16279800	-0.27836700	1.45312500
			O	2.28246500	-0.48129000	1.33565500
			N	1.31249000	-0.17554100	-1.40925700
			O	2.42488300	-0.33980100	-1.19090100
			N	-1.98958300	-0.96123700	-0.11589200
			O	-2.56837500	-1.93285900	0.06125800
			Ar	-0.85645100	2.30397100	0.05901200
	b	$^2A''$, C_s	Cu	-0.00596200	-0.29257600	0.00000000
			N	-1.94044300	-0.00396400	0.00000000
			O	-2.84750700	-0.70281500	0.00000000
			N	0.90091100	-0.55226800	1.71053200
			O	0.90091100	-1.35546000	2.52673600
			N	0.90091100	-0.55226800	-1.71053200
			O	0.90091100	-1.35546000	-2.52673600
			Ar	0.52826200	2.41967200	0.00000000
	c	^4A, C_1	Cu	-0.00997400	-0.00552500	0.65537400
			N	1.66159900	0.96509500	0.86091100
			O	2.42622300	1.40890000	0.13109000
			N	-1.69112800	0.95618500	0.81737600
			O	-2.43985200	1.39579600	0.06875100
			N	-0.00691500	-1.94229800	0.81726100
			O	0.00515300	-2.81077400	0.06901200
			Ar	0.03400900	0.01977600	-2.14586100
$[Cu(NO)_4]^+$	**a**	$^1A_1$, D_{2d}	Cu	0.00000000	0.00000000	0.00000000
			N	0.00000000	1.42539700	1.45608500
			O	0.00000000	1.25403600	2.58801000
			N	0.00000000	-1.42539700	1.45608500
			O	0.00000000	-1.25403600	2.58801000
			N	1.42539700	0.00000000	-1.45608500
			O	1.25403600	0.00000000	-2.58801000
			N	-1.42539700	0.00000000	-1.45608500
			O	-1.25403600	0.00000000	-2.58801000
	b	^3A, C_1	Cu	0.26284800	-0.03819000	-0.29483600
			N	-0.88623300	0.31937000	1.46201000
			O	-1.99515500	0.05593500	1.53944000
			N	-1.38771200	-0.57846600	-1.25955700
			O	-2.44655800	-0.71341600	-0.83933500
			N	1.65791900	-1.39629600	-0.14142100
			O	2.14155100	-2.02248800	0.68855400

			N	0.99097300	1.79323900	-0.57491400
			O	1.01925900	2.69779400	0.12976700
	c	D_{2h}	Cu	0.00000000	0.00000000	0.00000000
			N	0.00000000	1.48441600	1.49341700
			O	0.00000000	1.25427400	2.61401200
			N	0.00000000	-1.48441600	1.49341700
			O	0.00000000	-1.25427400	2.61401200
			N	0.00000000	-1.48441600	-1.49341700
			O	0.00000000	-1.25427400	-2.61401200
			N	0.00000000	1.48441600	-1.49341700
			O	0.00000000	1.25427400	-2.61401200
$[Cu(NO)_4Ar]^+$	**a**	^1A, C_1	Cu	-0.38822500	-0.29301500	0.05425900
			N	0.89948000	-0.77292500	1.56675800
			O	1.92479300	-1.26838000	1.44536800
			N	0.86871300	-1.18474700	-1.29105800
			O	1.87821100	-1.66934600	-1.05290900
			N	-1.25022400	1.52585300	0.25958400
			O	-2.37105200	1.76329600	0.25635200
			N	-2.26403200	-1.09755000	-0.31108000
			O	-3.25192000	-0.52078500	-0.27904500
			Ar	2.11337300	1.82026200	-0.33894900
	b	C_{2v}	Cu	0.00000000	0.00000000	0.43797600
			N	-1.48151500	1.49070900	0.47826600
			O	-1.25783400	2.61095600	0.55184100
			N	1.48151500	1.49070900	0.47826600
			O	1.25783400	2.61095600	0.55184100
			N	1.48151500	-1.49070900	0.47826600
			O	1.25783400	-2.61095600	0.55184100
			N	-1.48151500	-1.49070900	0.47826600
			O	-1.25783400	-2.61095600	0.55184100
			Ar	0.00000000	0.00000000	-2.43064800
	c	^1A, C_1	Cu	0.20207100	0.12421600	0.16736300
			N	2.31827000	0.47065600	0.25464000
			O	3.09181800	-0.34468700	0.04899300
			N	-0.17282200	1.91284700	-0.69428400
			O	0.49535000	2.84298000	-0.62993200
			N	0.56444700	-1.68144300	-0.61411300
			O	1.57167300	-2.22981600	-0.65111300
			N	-0.75759700	0.03267700	1.93855100
			O	-1.81811300	-0.32099300	2.19006500
			Ar	-2.56955400	-0.46251700	-1.03951100
$[Cu(NO)_5]^+$	**a**	^2A, C_1	Cu	-0.19657600	-0.09413600	0.00847900
			N	1.25818400	-1.58859100	-0.02910200
			O	2.37574000	-1.33625400	0.01788100

			N	0.90968900	0.91084900	-1.58672800
			O	2.04671000	0.81679400	-1.69284900
			N	-1.62411100	1.43511300	0.05944000
			O	-2.75856700	1.28144300	0.06171400
			N	-1.73092100	-1.49052200	-0.05317700
			O	-2.85054200	-1.24486100	-0.03823600
			N	0.96103100	0.85059900	1.57318400
			O	2.09711100	0.72135400	1.65258700
	b		Cu	0.42619100	-0.14458900	0.00069100
			N	-2.82173300	1.65788000	-0.44419300
			O	-3.77777300	1.18728100	-0.07263600
			N	0.33241200	-2.16346000	-0.54926400
			O	-0.34123300	-2.91356900	-0.00118100
			N	1.66902400	0.43157000	1.43783100
			O	2.61123600	1.08149300	1.33717900
			N	1.77311900	0.54695700	-1.37768500
			O	2.72416500	1.14601900	-1.15472600
			N	-1.52082700	0.19528700	0.11725900
			O	-2.26433100	-0.56179500	0.60290500
	c		Cu	0.02720800	0.05784800	-0.17735300
			N	1.04774900	-0.13648100	1.58096400
			O	2.14816200	-0.39882300	1.77008400
			N	2.00670500	-0.30385700	-1.10681200
			O	2.98100300	-0.53039300	-0.55698700
			N	-0.12407400	1.96714400	-0.82127200
			O	-0.69786300	2.83236100	-0.33013200
			N	-0.86465800	-1.51426600	-1.00283900
			O	-1.79654400	-2.09785400	-0.66600800
			N	-1.98636000	0.41102100	0.83884300
			O	-2.80282800	-0.38560600	0.87317500
	d		Cu	-0.70068800	0.15637500	-0.33468900
			N	2.35082200	0.78552000	0.78354700
			O	3.24954000	0.09965500	0.73141700
			N	-0.23119900	1.92083800	-1.01036700
			O	0.61033100	2.68871100	-0.85501300
			N	-0.56220700	-1.38721900	-1.57810200
			O	0.12835400	-2.30024600	-1.48389400
			N	0.56464300	-0.82426900	1.02498700
			O	1.12313000	-1.80617400	0.77497900
			N	-2.32074800	0.24771400	0.84956300
			O	-2.39751000	0.10143400	1.98483300

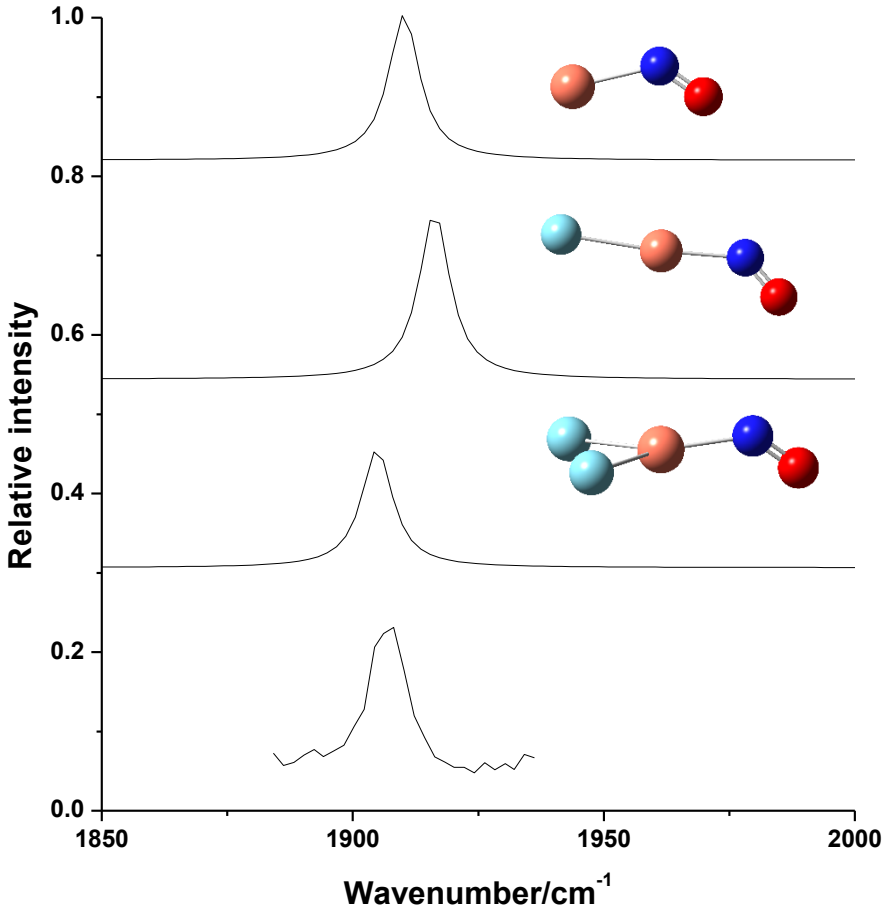
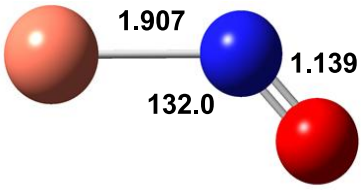
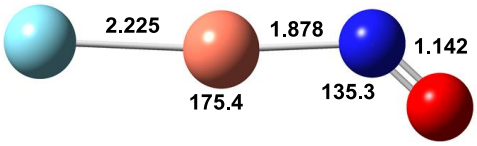


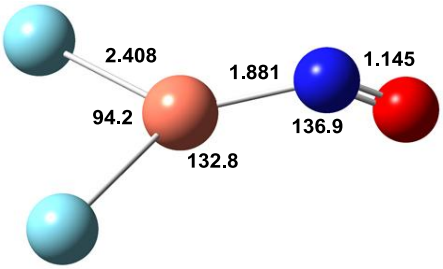
Figure S1. Experimental IR spectrum of $[Cu(NO)Ar_2]^+$ (a) and the simulated IR spectra of $[Cu(NO)Ar_2]^+$ (b), $[Cu(NO)Ar]^+$ (c), and $Cu(NO)^+$ (d).



Cu(NO)$^+$, C_s, ^{2}A'

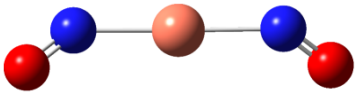


[Cu(NO)Ar]$^+$, C_s, ^{2}A'

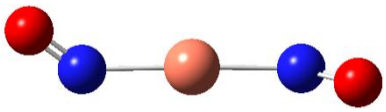


[Cu(NO)Ar$_2$]$^+$, C_s, ^{2}A'

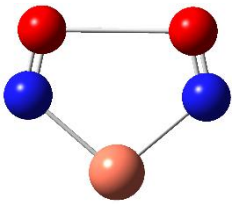
Figure S2. Optimized geometries (bond lengths in angstrom and bond angles in degrees) and relative energies (kcal/mol) of the [Cu(NO)Ar$_n$]$^+$ (n=0, 1, 2) cation complexes.



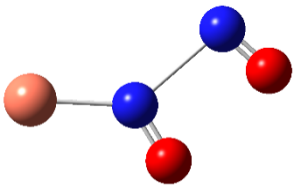
(a) [Cu(NO)$_2$]$^+$
ΔE=0.0, C_2, ^{1}A



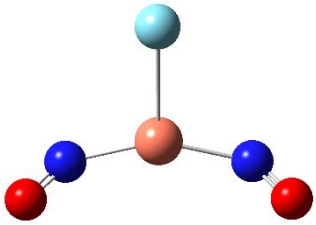
(b) [Cu(NO)$_2$]$^+$
ΔE=0.2, C_2, ^{3}B



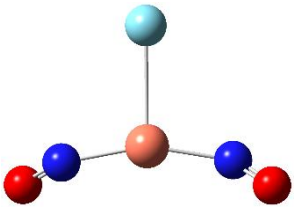
(c) [Cu(NO)$_2$]$^+$
ΔE=6.7, C_{2v}, ^{1}A$_1$



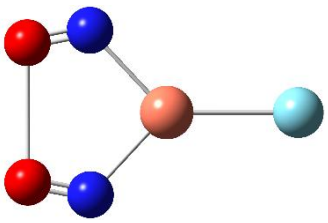
(d) [Cu(NO)$_2$]$^+$
ΔE=12.9, C_s, ^{1}A'



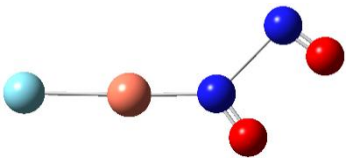
(a) [Cu(NO)$_2$Ar]$^+$
ΔE=0.0, C_s, ^{1}A



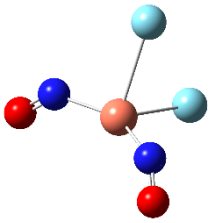
(b) [Cu(NO)$_2$ Ar]$^+$
ΔE=0.6, C_2, ^{3}B



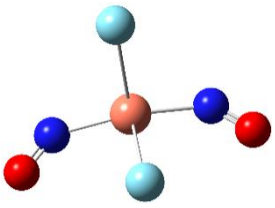
(c) [Cu(NO)$_2$ Ar]$^+$
ΔE=1.3, C_{2v}, ^{1}A$_1$



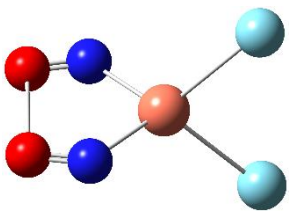
(d) [Cu(NO)$_2$ Ar]$^+$
ΔE=4.5, C_s, ^{1}A'



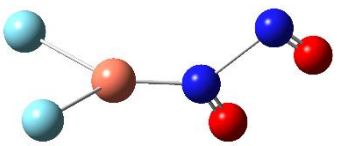
(a) [Cu(NO)$_2$Ar$_2$]$^+$
ΔE=0.0, C_s, ^{1}A



(b) [Cu(NO)$_2$Ar$_2$]$^+$
ΔE=0.7, C_s, ^{3}A"

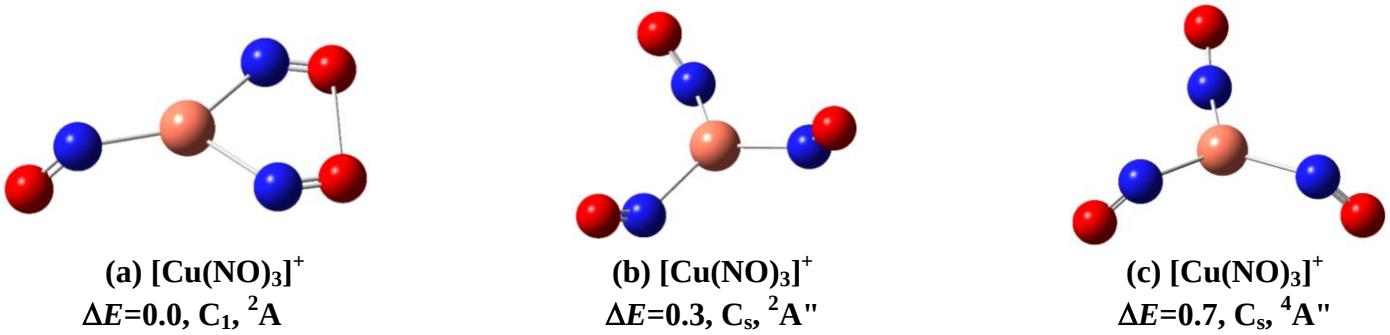


(c) [Cu(NO)$_2$Ar$_2$]$^+$
ΔE=0.7, C_{2v}, ^{1}A$_?$



(d) [Cu(NO)$_2$Ar$_2$]$^+$
ΔE=5.9, C_s, ^{1}A'

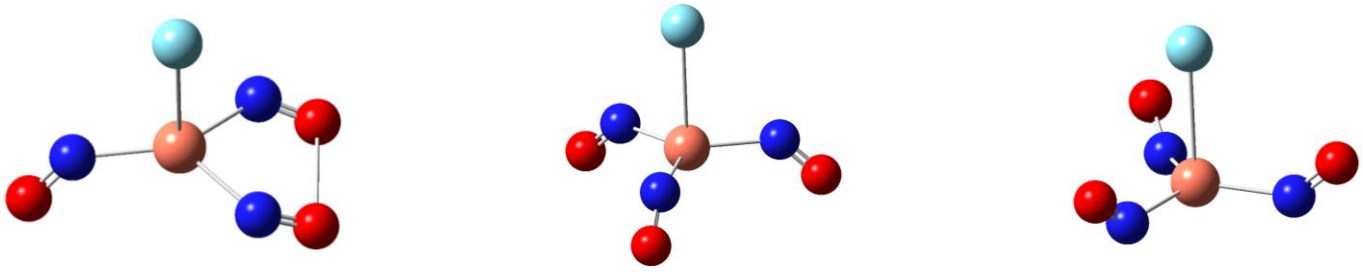
Figure S3. Optimized geometries and relative energies (in kcal/mol) of the isomers of the $[CuNO_2]^+$, $[CuNO_2Ar]^+$, and $[CuNO_2Ar_2]^+$ cation complexes.



(a) $[Cu(NO)_3]^+$
ΔE=0.0, C_1, ^{2}A

(b) $[Cu(NO)_3]^+$
ΔE=0.3, C_s, ^{2}A"

(c) $[Cu(NO)_3]^+$
ΔE=0.7, C_s, ^{4}A"



(a) $[Cu(NO)_3Ar]^+$
ΔE=0.0, C_1, ^{2}A

(b) $[Cu(NO)_3Ar]^+$
ΔE=0.2, C_s, ^{2}A"

(c) $[Cu(NO)_3Ar]^+$
ΔE=1.6, C_1, ^{4}A

Figure S4. Optimized geometries and relative energies (in kcal/mol) of the isomers of the $[CuNO_3]^+$ and $[CuNO_3Ar]^+$ cation complexes.

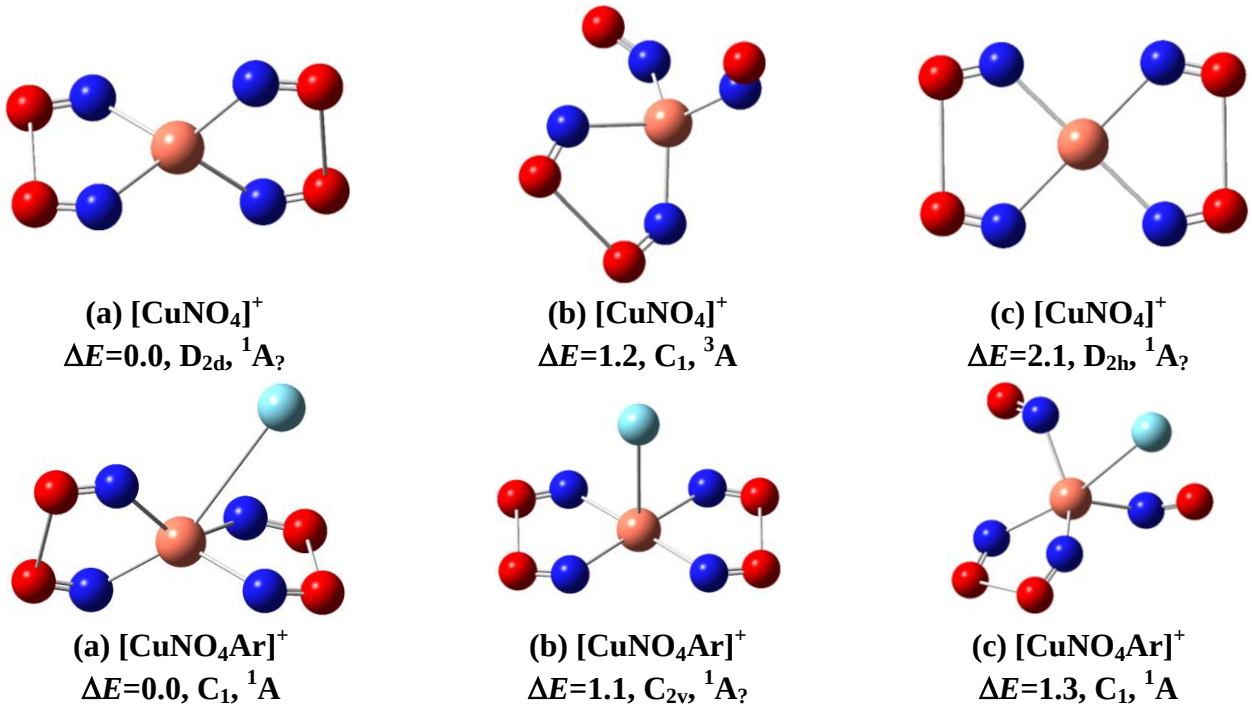


Figure S5. Optimized geometries and relative energies (in kcal/mol) of the isomers of the $[CuNO_4]^+$ and $[CuNO_4Ar]^+$ cation complexes.