

Appendix A

QTAIM VALUES OF DOUBLE METAL DOPED GOLD CLUSTERS

Table A.1 Calculated values of selected bond properties of Au-Au and Au-Be bonds of different Au_nBe₂ clusters.

Cluster	Interaction	ρ	$\nabla^2 \rho$	H(r)	G(r)/ ρ
Neutral					
Au₅	Au2 - Au4	0.04	0.096	-0.009	0.822
	Au1 - Au2	0.05	0.112	-0.014	0.848
	Au2 - Au3	0.047	0.108	-0.013	0.848
	Au1 - Au4	0.055	0.116	-0.017	0.841
	Au3 - Au4	0.04	0.096	-0.009	0.822
	Au3 - Au5	0.05	0.112	-0.014	0.848
	Au4 - Au5	0.055	0.116	-0.017	0.84
Au₃-Be₂	Au1 - Be5	0.046	0.088	-0.015	0.812
	Au3 - Be5	0.046	0.088	-0.015	0.812
	Au1 - Be4	0.051	0.112	-0.017	0.887
	Au3 - Be4	0.051	0.112	-0.017	0.887
	Au2 - Be5	0.065	0.114	-0.029	0.885
Cationic					
Au₆	Au1 - Au3	0.045	0.103	-0.012	0.828
	Au1 - Au2	0.054	0.106	-0.016	0.799
	Au2 - Au3	0.055	0.120	-0.017	0.854
	Au3 - Au5	0.027	0.071	-0.002	0.751
	Au3 - Au4	0.052	0.109	-0.016	0.825
	Au1 - Au5	0.045	0.103	-0.012	0.828

	Au4 - Au5	0.052	0.109	-0.016	0.825
	Au1 - Au6	0.054	0.106	-0.016	0.799
	Au5 - Au6	0.055	0.120	-0.017	0.854
Au₄-Be₂	Au4 - Be6	0.048	0.082	-0.018	0.79
	Au4 - Be5	0.048	0.082	-0.018	0.79
	Au2 - Be5	0.054	0.096	-0.02	0.822
	Au3 - Be5	0.065	0.111	-0.029	0.88
	Au1 - Be6	0.065	0.111	-0.029	0.88
	Au2 - Be6	0.054	0.096	-0.02	0.822
Anionic					
Au₆	Au1 - Au3	0.045	0.104	-0.012	0.838
	Au1 - Au2	0.048	0.102	-0.013	0.814
	Au2 - Au3	0.048	0.102	-0.013	0.814
	Au3 - Au5	0.045	0.104	-0.012	0.838
	Au3 - Au4	0.048	0.102	-0.013	0.814
	Au1 - Au5	0.045	0.104	-0.012	0.838
	Au4 - Au5	0.048	0.102	-0.013	0.814
	Au1 - Au6	0.048	0.102	-0.013	0.814
	Au5 - Au6	0.048	0.102	-0.013	0.814
Au₄-Be₂	Au2 - Be6	0.048	0.123	-0.015	0.953
	Au2 - Be5	0.048	0.123	-0.015	0.953
	Au4 - Be6	0.048	0.123	-0.015	0.953
	Au4 - Be5	0.048	0.123	-0.015	0.953
	Au3 - Be5	0.057	0.121	-0.022	0.922

Appendix B

**VIBRATIONAL FREQUENCIES OF
DIFFERENT STRUCTURES OF HFE-365MCF3
AND HFE-7000 (i-C₃F₇OCH₃)**

Table B.1. Harmonic vibrational frequencies of reactants, reaction complexes, transition states, product complexes and products at M06-2X level of theory using 6-31+G(d,p) basis set.

Species	Vibrational Frequencies (cm ⁻¹)
Reactant	32, 57, 79, 112, 220, 225, 246, 321, 348, 351, 376, 448, 533, 595, 609, 740, 838, 993, 1014, 1092, 1181, 1194, 1217, 1255, 1270, 1280, 1310, 1328, 1420, 1459, 1487, 1500, 1503, 1523, 3034, 3042, 3088, 3099, 3176
OH	3758
RC1	24, 55, 85, 95, 100, 121, 155, 219, 224, 251, 299, 322, 352, 355, 375, 381, 450, 533, 595, 610, 740, 836, 996, 1012, 1092, 1181, 1189, 1213, 1252, 1275, 1276, 1311, 1327, 1419, 1457, 1488, 1500, 1501, 1518, 3041, 3052, 3103, 3112, 3183, 3761
RC2a	22, 40, 61, 82, 95, 124, 13, 215, 225, 254, 320, 349, 377, 384, 450, 527, 552, 596, 613, 741, 839, 997, 1015, 1094, 1180, 1197, 1218, 1258, 1273, 1282, 1316, 1331, 1423, 1462, 1487, 1501, 1504, 1521, 3044, 3053, 3104, 3114, 3191, 3693
TS1	944i, 38, 65, 88, 107, 122, 126, 214, 223, 240, 255, 314, 323, 357, 379, 440, 534, 594, 608, 716, 749, 845, 947, 1022, 1080, 1106, 1182, 1196, 1254, 1265, 1275, 1297, 1311, 1397, 1417, 1449, 1491, 1501, 1513, 1576, 3053, 3065, 3127, 3189, 3775
TS2a	1334i, 36, 55, 62, 84, 115, 118, 222, 247, 273, 304, 330, 339, 345, 371, 447, 531, 594, 602, 733, 744, 833, 904, 990, 1039, 1112, 1155, 1209, 1220, 1268, 1273, 1281, 1284, 1314, 1327, 1418, 1454, 1488, 1511, 1557, 3057, 3060, 3111, 3141, 3765

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Species	Vibrational Frequencies (cm ⁻¹)
TS2b	868i, 22, 41, 64, 114, 125, 151, 223, 245, 264, 318, 323, 348, 365, 384, 450, 533, 595, 609, 736, 749, 838, 953, 1002, 1019, 1095, 1201, 1212, 1253, 1275, 1281, 1313, 1332, 1373, 1419, 1440, 1463, 1480, 1504, 1669, 3062, 3064, 3121, 3191, 3777
PC1	34, 53, 90, 108, 125, 135, 162, 167, 198, 218, 249, 274, 332, 351, 359, 373, 394, 443, 537, 570, 609, 629, 747, 867, 1020, 1075, 1119, 1181, 1195, 1266, 1308, 1335, 1419, 1464, 1497, 1516, 1552, 1619, 3075, 3167, 3203, 3234, 3861, 3987
PC2a	36, 51, 62, 96, 130, 157, 175, 218, 236, 250, 294, 312, 324, 360, 364, 383, 449, 500, 534, 595, 610, 641, 741, 840, 992, 1023, 1098, 1208, 1222, 1268, 1277, 1311, 1317, 1332, 1420, 1462, 1493, 1618, 3082, 3149, 3183, 3332, 3859, 3983
PC2b	36, 38, 70, 112, 124, 141, 160, 221, 240, 251, 305, 324, 333, 353, 366, 385, 410, 448, 534, 595, 610, 690, 743, 841, 992, 1019, 1096, 1213, 1221, 1267, 1278, 1312, 1328, 1338, 1419, 1465, 1491, 1497, 1619, 3080, 3164, 3308, 3842, 3958
H ₂ O	1596, 3887, 4012
P1	29, 58, 83, 112, 160, 215, 248, 328, 337, 350, 375, 428, 537, 544, 607, 619, 747, 872, 1024, 1104, 1141, 1175, 1188, 1262, 1272, 1304, 1328, 1419, 1464, 1501, 1508, 1547, 3064, 3143, 3199, 3220
P2	44, 63, 92, 119, 222, 247, 318, 324, 345, 362, 380, 447, 534, 595, 610, 677, 742, 842, 988, 1025, 1098, 1208, 1220, 1269, 1271, 1313, 1326, 1331, 1421, 1460, 1492, 1504, 3065, 3123, 3161, 3329

Table B.2 Harmonic vibrational frequencies of reactants, transition states and products at M06-2X level of theory using 6-31+G(d,p) basis set.

Species	Vibrational Frequencies (cm ⁻¹)
CF ₃ CF ₂ CH(O [•])OCH ₃	52, 71, 100, 126, 171, 224, 233, 260, 312, 332, 354, 387, 450, 537, 583, 630, 639, 744, 824, 976, 1068, 1109, 1149, 1185, 1196, 1242, 1264, 1285, 1290, 1303, 1342, 1422, 1485, 1499, 1520, 2899, 3049, 3135, 3195
TS3	450i, 48, 66, 112, 152, 160, 200, 218, 230, 285, 318, 363, 371, 436, 530, 595, 621, 700, 755, 839, 969, 1040, 1171, 1187, 1200, 1234, 1262, 1313, 1318, 1348, 1409, 1474, 1497, 1513, 1565, 3043, 3090, 3171, 3206
TS4	1029i, 56, 72, 103, 121, 150, 223, 241, 287, 309, 339, 354, 400, 450, 539, 578, 585, 601, 672, 754, 786, 865, 985, 1118, 1179, 1199, 1233, 1247, 1283, 1303, 1360, 1421, 1481, 1492, 1501, 1728, 30830, 3170, 3219
TS5	1284i, 37, 51, 61, 75, 120, 149, 164, 198, 220, 235, 257, 286, 309, 338, 357, 401, 465, 512, 538, 594, 654, 728, 758, 833, 979, 1050, 1132, 1180, 1193, 1202, 1241, 1256, 1278, 1296, 1302, 1422, 1427, 1497, 1508, 1599, 1693, 3070, 3147, 3216
CF ₃ CF ₂ CH ₂ OCH ₂ O [•]	33, 63, 67, 99, 160, 222, 243, 284, 333, 345, 372, 447, 525, 591, 595, 628, 746, 813, 861, 990, 1005, 1083, 1108, 1192, 1218, 1239, 1273, 1279, 1313, 1327, 1356, 1401, 1418, 1464, 1510, 2913, 3054, 3057, 3131

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Species	Vibrational Frequencies (cm ⁻¹)
TS6	1047i, 32, 63, 74, 99, 213, 221, 241, 245, 329, 346, 372, 447, 527, 542, 594, 596, 606, 712, 780, 882, 977, 1016, 1096, 1115, 1211, 1232, 1273, 1278, 1314, 1326, 1373, 1415, 1457, 1497, 1701, 3090, 3098, 3161
TS7	1539i, 26, 45, 65, 67, 99, 143, 169, 183, 228, 268, 287, 327, 368, 441, 450, 524, 562, 585, 595, 624, 746, 823, 955, 1037, 1043, 1066, 1170, 1198, 1224, 1256, 1272, 1277, 1314, 1345, 1363, 1410, 1447, 1492, 1618, 1699, 2962, 3070, 3162
CF ₃ CF ₂ C(O)OCH ₃	14, 82, 115, 121, 134, 218, 239, 282, 310, 355, 419, 428, 541, 592, 670, 755, 797, 847, 987, 1117, 1182, 1203, 1235, 1289, 1305, 1408, 1429, 1493, 1502, 1902, 3100, 3191, 3223
CF ₃ C•F ₂	60, 205, 220, 364, 422, 515, 591, 611, 715, 852, 1170, 1254, 1295, 1344, 1457
CH ₃ OC(O)H	126, 320, 353, 790, 987, 1060, 1184, 1204, 1285, 1404, 1478, 1492, 1504, 1860, 3092, 3121, 3177, 3206
CF ₃ CF ₂ CH ₂ OC(O)H	30, 64, 81, 99, 220, 237, 246, 323, 329, 360, 372, 447, 527, 596, 602, 715, 784, 888, 977, 1021, 1049, 1100, 1215, 1255, 1274, 1281, 1316, 1328, 1404, 1418, 1458, 1500, 1869, 3116, 3176, 3177
HO• ₂	1287, 1459, 3713
O ₂	1776

Table B.3 Harmonic vibrational frequencies of reactants, reaction complexes, transition states, product complexes and products at M06-2X/6-31+G(d,p) level of theory.

Species	Vibrational Frequencies (cm ⁻¹)
i-C ₃ F ₇ OCH ₃	56, 81, 117, 166, 189, 223, 241, 276, 299, 323, 348, 378, 389, 460, 538, 556, 570, 616, 680, 744, 791, 1023, 1065, 1162, 1184, 1209, 1245, 1269, 1277, 1306, 1323, 1387, 1419, 1494, 1508, 1520, 3089, 3179, 3208
H	3758
RC1a	36, 52, 66, 75, 129, 137, 160, 197, 229, 251, 278, 298, 302, 328, 349, 377, 390, 401, 460, 538, 557, 567, 617, 683, 744, 791, 1018, 1061, 1166, 1188, 1211, 1244, 1270, 1275, 1305, 1318, 1385, 1419, 1498, 1509, 1524, 3091, 3186, 3215, 3759
RC1b	41, 54, 67, 82, 103, 148, 153, 178, 187, 228, 260, 281, 288, 309, 326, 349, 382, 389, 461, 539, 557, 569, 616, 681, 744, 790, 1018, 1060, 1157, 1188, 1211, 1244, 1260, 1279, 1303, 1326, 1383, 1419, 1498, 1512, 1541, 3096, 3191, 3206, 3763
TS1a	1136i, 44, 57, 81, 101, 114, 157, 183, 193, 234, 272, 297, 322, 343, 356, 384, 394, 459, 537, 558, 569, 616, 682, 741, 772, 792, 862, 1033, 1089, 1174, 1189, 1199, 1248, 1270, 1287, 1307, 1330, 1367, 1387, 1423, 1491, 1502, 3138, 3233, 3805
TS1b	1381i, 25, 48, 71, 75, 113, 156, 173, 228, 264, 267, 290, 321, 326, 345, 366, 385, 458, 538, 556, 568, 610, 668, 733, 763, 809, 870, 1033, 1082, 1160, 1181, 1241, 1252, 1266, 1278, 1303, 1315, 1326, 1388, 1420, 1480, 1536, 3117, 3217, 3767
PC1a	24, 60, 61, 76, 128, 137, 161, 205, 228, 242, 261, 278, 279, 304, 324, 331, 348, 386, 394, 462, 539, 556, 569, 619, 685, 722, 745, 793, 1032, 1119, 1185, 1206, 1248, 1274, 1277, 1315, 1322, 1384, 1423, 1479, 1598, 3193, 3348, 3873, 3999
PC1b	24, 49, 61, 70, 88, 137, 162, 171, 190, 200, 234, 244, 275, 301, 324, 332, 350, 387, 396, 459, 540, 557, 569, 615, 683, 731, 747, 793, 1034, 1128, 1184, 1209, 1253, 1270, 1278, 1312, 1333, 1381, 1422, 1482, 1612, 3190, 3340, 3859, 3985
H ₂ O	1596, 3887, 4012

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Species	Vibrational Frequencies (cm ⁻¹)
HCl	3031
i-C ₃ F ₇ OC•H ₂	52, 73, 124, 169, 193, 225, 263, 277, 297, 325, 349, 385, 392, 460, 538, 555, 570, 616, 676, 683, 745, 793, 1033, 1124, 1180, 1206, 1250, 1274, 1281, 1314, 1327, 1382, 1422, 1482, 3195, 3348
i-C ₃ F ₇ OCH ₂ O•	44, 65, 95, 144, 161, 175, 223, 265, 278, 309, 324, 350, 384, 459, 537, 55, 561, 593, 620, 685, 743, 789, 841, 1003, 1052, 1129, 1168, 1200, 1245, 1260, 1275, 1317, 1321, 1364, 1385, 1409, 1425, 3026, 3079
TS2	540i, 43, 58, 73, 80, 108, 148, 220, 234, 281, 317, 329, 336, 348, 379, 461, 537, 556, 564, 591, 620, 697, 736, 797, 963, 1011, 1079, 1119, 1229, 1246, 1274, 1300, 1322, 1326, 1352, 1369, 1747, 2649, 3091
TS3	1019i, 55, 84, 96, 154, 167, 182, 223, 269, 291, 311, 330, 360, 384, 455, 531, 539, 543, 569, 594, 614, 647, 726, 787, 821, 1043, 1081, 1096, 1183, 1219, 1242, 1283, 1317, 1327, 1357, 1375, 1405, 1756, 3139
TS4	1724i, 27, 50, 57, 80, 114, 130, 160, 166, 178, 232, 271, 293, 325, 341, 354, 376, 428, 471, 529, 539, 557, 569, 572, 641, 725, 748, 816, 970, 1045, 1066, 1159, 1186, 1235, 1251, 1273, 1298, 1310, 1328, 1373, 1383, 1418, 1623, 1687, 3028
C ₃ F ₇ O•	32, 88, 149, 228, 230, 270, 310, 323, 336, 391, 462, 539, 551, 559, 616, 684, 729, 802, 977, 1141, 1178, 1227, 1265, 1289, 1320, 1334, 1338
CH ₂ O•	1212, 1275, 1547, 1881, 2976, 3049
i-C ₃ F ₇ OC(O)H	38, 62, 76, 133, 148, 205, 225, 259, 284, 320, 338, 358, 373, 426, 524, 538, 563, 567, 642, 736, 761, 845, 1024, 1041, 1079, 1194, 1244, 1255, 1286, 1321, 1332, 1386, 1420, 1432, 1932, 3168
HO• ₂	1266, 1459, 3710
TS5	1178i, 29, 56, 66, 80, 95, 139, 162, 195, 233, 260, 281, 290, 323, 340, 359, 374, 406, 490, 537, 563, 566, 619, 707, 739, 756, 790, 855, 1006, 1033, 1103, 1193, 1255, 1261, 1283, 1324, 1326, 1381, 1417, 1505, 1964, 3778
TS6	1114i, 40, 53, 61, 78, 96, 138, 159, 230, 255, 270, 294, 320, 340, 349, 362, 376, 446, 538, 549, 564, 570, 650, 737, 762, 843, 933, 1035, 1106, 1133, 1192, 1251, 1261, 1290, 1329, 1334, 1377, 1416, 1997
C ₃ F ₇ OC(O)	36, 64, 90, 138, 147, 204, 230, 253, 282, 322, 337, 356, 370, 427, 520, 538, 562, 569, 641, 735, 757, 834, 1017, 1063, 1183, 1246, 1261, 1284, 1328, 1330, 1385, 1414, 2000