

# Supplementary Materials for Article: The Boundary Between Two Modes of Gas Evolution: Oscillatory (H<sub>2</sub> and O<sub>2</sub>) and Conventional Redox (O<sub>2</sub> only), in The Hydrocarbon/H<sub>2</sub>O<sub>2</sub>/Cu(II)/CH<sub>3</sub>CN System

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Orca—an ab initio, DFT, and semiempirical SCF-MO package—version 3.0.1 was used for all DFT calculations in the BPE0/TZVPP level of theory. The ChemCraft 1.7 program was used to create input files, visualize and design the calculation results.

**Table S1.** The Charge, Spin state, Energy and XYZ coordinates of all atoms of all structures optimized by the DFT method.

## Type of chemical structure (Charge;Spin state), Energy

### CuH (20)



Molecule (0;1), E = -1640.833185884078 E<sub>h</sub>

Radical Anion (-1;2), E = -1640.825562232613 E<sub>h</sub>

Cu	0.000000000	0.000000000	0.158466000	Cu	0.000000000	0.000000000	0.097687000
H	0.000000000	0.000000000	1.633212000	H	0.000000000	0.000000000	1.693991000

### Cu<sub>2</sub> (21)

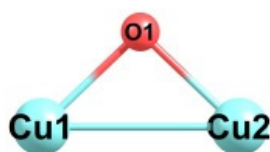


Molecule (0;1), E = -3280.540332075323 E<sub>h</sub>

Radical Anion (-1;2), E = -3280.557003438048 E<sub>h</sub>

Cu	0.000000000	0.000000000	-1.133974000	Cu	0.000000000	0.000000000	-1.190713000
Cu	0.000000000	0.000000000	1.133974000	Cu	0.000000000	0.000000000	1.190713000

### Cu<sub>2</sub>O (22)



Molecule (0;1), E = -3355.687224138422 E<sub>h</sub>

Radical Anion (-1;2), E = -3355.709345013066 E<sub>h</sub>

Cu	-1.274310000	0.000000000	-0.086185000	Cu	-1.239288000	0.000000000	-0.116458000
O	-0.000000000	0.000000000	1.136921000	O	0.000001000	0.000000000	1.197466000
Cu	1.274310000	0.000000000	-0.086185000	Cu	1.239287000	0.000000000	-0.116457000

(Single point calculations)

Atom (0;2), E = -1640.236451203338 E<sub>h</sub>

Cu	0.000000000	0.000000000	0.000000000
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Cu (23)



(Single point calculations)

Anion (-1;1), E = -1640.261078219124 E<sub>h</sub>

Cu	0.000000000	0.000000000	0.000000000
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CuCl (24)



Molecule (0;1), E = -2100.368056439018 E<sub>h</sub>

Cu	-0.005694000	0.000021000	-0.132240000
Cl	2.070095000	-0.000012000	-0.132202000

Radical Anion (-1;2), E = -2100.401477462000 E<sub>h</sub>

Cu	-0.085553000	0.000022000	-0.132241000
Cl	2.149954000	-0.000013000	-0.132201000

Cl (25)



(Single point calculations)

Atom (0;2), E = -459.996618462930 E<sub>h</sub>

Cl	0.000000000	0.000000000	0.000000000
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(Single point calculations)

Anion (-1;1), E = -460.116771209037 E<sub>h</sub>

Cl	0.000000000	0.000000000	0.000000000
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CuCl<sub>2</sub> (26)



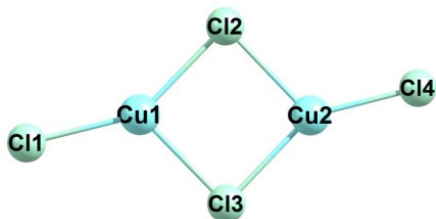
Molecule (0;2), E = -2560.458515677480 E<sub>h</sub>

Cu	0.000000000	0.000021000	-0.132240000
Cl	2.064401000	-0.000012000	-0.132202000
Cl	-2.064401000	-0.000009000	-0.132198000

Radical Anion (-1;1), E = -2560.605611152270 E<sub>h</sub>

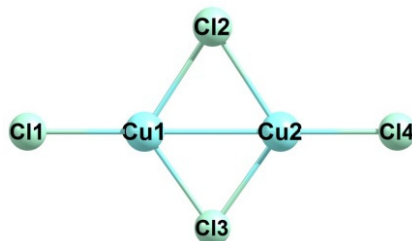
Cu	-0.000000000	0.000018000	-0.132236000
Cl	2.141315000	-0.000011000	-0.132204000
Cl	-2.141315000	-0.000008000	-0.132200000

Cu<sub>2</sub>Cl<sub>4</sub> (27)



Molecule (0;3), E = -5120.975980754558 E<sub>h</sub>

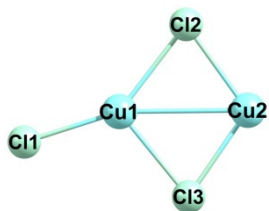
Cu	1.540707000	-0.258590000	0.000134000
Cl	3.620470000	-0.086999000	-0.000901000
Cl	-0.252139000	-1.598312000	0.000767000
Cu	-1.540707000	0.258590000	0.000134000
Cl	0.252139000	1.598312000	0.000767000
Cl	-3.620470000	0.086999000	-0.000901000



Radical Anion (-1;2), E = -5121.134650902112 E<sub>h</sub>

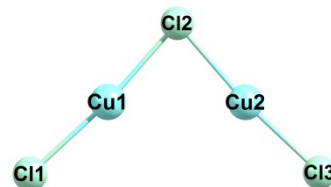
Cu	1.263098000	-0.000000000	-0.000179000
Cl	3.433506000	0.000000000	0.000152000
Cl	0.000000000	-1.886576000	-0.000027000
Cu	-1.263098000	-0.000000000	-0.000009000
Cl	0.000000000	1.886576000	-0.000027000
Cl	-3.433506000	0.000000000	0.000090000

### Cu<sub>2</sub>Cl<sub>3</sub> (28)



Molecule (0;2), E = -4660.897876026251 E<sub>h</sub>

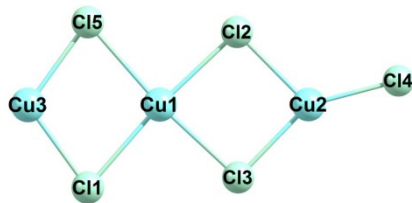
Cu	1.390455000	-0.266995000	0.000106000
Cl	3.476029000	-0.025404000	-0.000547000
Cl	-0.321355000	-1.780479000	0.000517000
Cu	-1.239301000	0.222337000	0.000412000
Cl	0.314642000	1.763543000	0.000413000



Radical Anion (-1;1), E = -4661.057944058063 E<sub>h</sub>

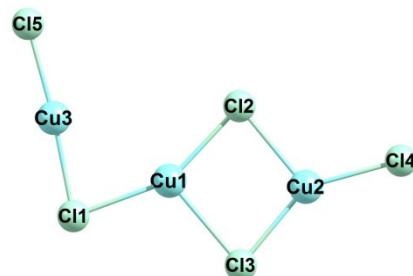
Cu	-1.428388000	0.000000000	0.132909000
Cl	0.000001000	-0.000000000	1.773292000
Cl	-2.974429000	-0.000000000	-1.318006000
Cu	1.428393000	0.000000000	0.132901000
Cl	2.974423000	-0.000000000	-1.318022000

### Cu<sub>3</sub>Cl<sub>5</sub> (29)



Molecule (0;3), E = -7221.407385765084 E<sub>h</sub>

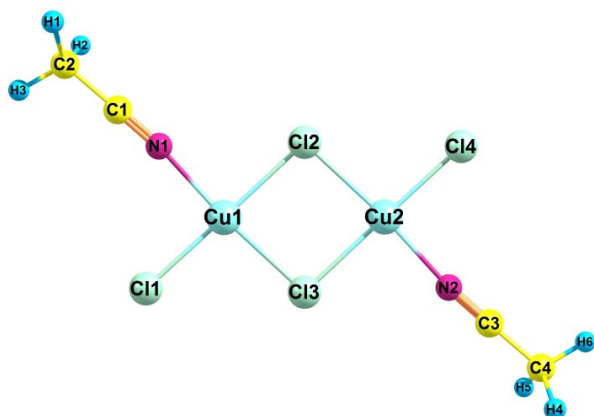
Cu	1.614419000	-0.000066000	0.000290000
Cl	3.155465000	-0.000144000	1.774112000
Cl	-0.069112000	0.000018000	-1.577042000
Cu	-1.642781000	-0.000035000	0.011054000
Cl	-0.082650000	0.000406000	1.592306000
Cl	-3.670439000	-0.000199000	-0.508175000
Cl	3.155731000	0.000256000	-1.778300000
Cu	4.414722000	-0.000234000	-0.001180000



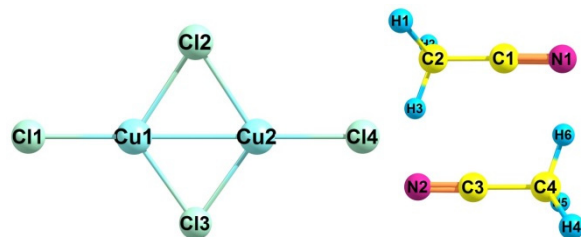
Radical Anion (-1;2), E = -7221.579242854321 E<sub>h</sub>

Cu	1.206512000	0.001468000	0.503581000
Cl	3.164243000	0.002147000	1.553343000
Cl	-0.069459000	-0.000084000	-1.308841000
Cu	-1.740017000	-0.001181000	0.221588000
Cl	-0.581321000	-0.001264000	2.097757000
Cl	-3.708035000	-0.000903000	-0.628927000
Cl	4.722316000	-0.000694000	-2.432275000
Cu	3.881116000	0.000513000	-0.493163000

**Cu<sub>2</sub>Cl<sub>4</sub>·2AN (30)**



Radical Anion 30 = Radical Anion 27 + 2 Molecule 2



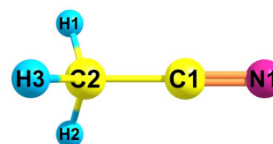
Radical Anion 27

2 Molecule 2

Molecule (0;3), E = -5386.306768478984 E<sub>h</sub>

Cu	0.612586000	-1.567265000	-0.000116000
Cl	2.581126000	-2.540138000	-0.000190000
Cl	-1.463773000	-0.566468000	-0.000180000
Cu	-0.612587000	1.567266000	-0.000357000
Cl	1.463773000	0.566468000	-0.000326000
Cl	-2.581126000	2.540138000	-0.000067000
C	-0.680033000	-4.435088000	0.000053000
N	-0.284845000	-3.363063000	-0.000010000
C	-1.162580000	-5.794759000	0.000133000
H	-1.770189000	-5.969337000	0.888426000
H	-1.770167000	-5.969450000	-0.888153000
H	-0.315750000	-6.481672000	0.000188000
C	0.680033000	4.435088000	-0.000004000
N	0.284845000	3.363063000	-0.000129000
C	1.162581000	5.794759000	0.000153000
H	1.770107000	5.969316000	0.888506000
H	1.770249000	5.969471000	-0.888073000
H	0.315750000	6.481671000	0.000146000

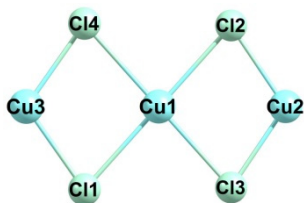
Radical Anion 30 (-1;2), E = -5386.419549320808 E<sub>h</sub>



Molecule 2 (0;1), E = -132.642449209348 E<sub>h</sub>

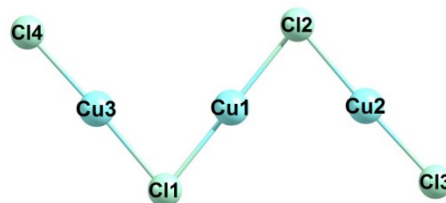
C	-0.000008000	0.000030000	0.163857000
N	-0.000071000	-0.000030000	1.312892000
C	-0.000026000	0.000006000	-1.285436000
H	0.511815000	0.886647000	-1.660733000
H	0.511816000	-0.886651000	-1.660696000
H	-1.023527000	-0.000002000	-1.660484000

### Cu<sub>3</sub>Cl<sub>4</sub> (31)



Molecule (0;2), E = -6761.320975170130 E<sub>h</sub>

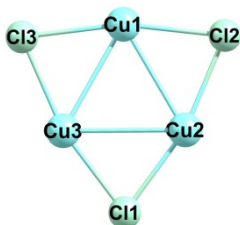
Cu	0.000000000	0.000000000	0.000012000
Cl	1.593748000	1.784916000	-0.000002000
Cl	-1.593748000	-1.784915000	-0.000002000
Cu	-2.816803000	0.000000000	0.000001000
Cl	-1.593748000	1.784916000	-0.000005000
Cl	1.593748000	-1.784916000	-0.000005000
Cu	2.816803000	-0.000000000	0.000001000



Radical Anion (-1;1), E = -6761.504989147751 E<sub>h</sub>

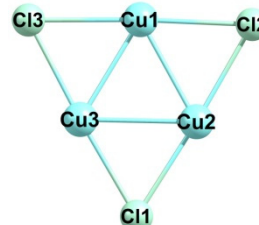
Cu	1.513908000	-0.002271000	0.023094000
Cl	3.283837000	-0.001504000	1.277750000
Cl	-0.252468000	-0.003060000	-1.233972000
Cu	-1.152019000	-0.000549000	0.745256000
Cl	-2.105485000	0.002240000	2.630952000
Cl	5.118268000	0.004375000	-2.596373000
Cu	4.177349000	0.001674000	-0.704716000

### Cu<sub>3</sub>Cl<sub>3</sub> (32)



Molecule (0;1), E = -6301.307588396459 E<sub>h</sub>

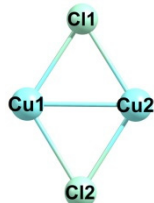
Cu	0.000000000	-0.000004000	1.609911000
Cl	-0.000000000	-0.000001000	-2.400857000
Cu	1.303557000	0.000001000	-0.647819000
Cl	2.169351000	0.000002000	1.357469000
Cl	-2.169351000	0.000002000	1.357469000
Cu	-1.303557000	0.000001000	-0.647819000



Radical Anion (-1;2), E = -6301.316250677407 E<sub>h</sub>

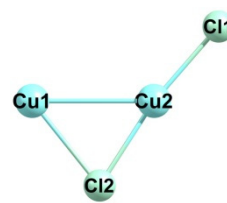
Cu	-0.000000000	0.000001000	1.525426000
Cl	0.000000000	0.000001000	-2.626425000
Cu	1.228154000	-0.000001000	-0.605191000
Cl	2.363945000	0.000000000	1.469867000
Cl	-2.363945000	0.000000000	1.469867000
Cu	-1.228154000	-0.000001000	-0.605191000

### Cu<sub>2</sub>Cl<sub>2</sub> (33)



Molecule (0;1), E = -4200.819250735715 E<sub>h</sub>

Cu	0.319788000	-1.151112000	0.000039000
Cl	-1.851790000	-0.511897000	-0.000039000
Cu	-0.319788000	1.151112000	0.000039000
Cl	1.851790000	0.511897000	-0.000039000



Radical Anion (-1;2), E = -4200.869614232684 E<sub>h</sub>

Cu	1.275495000	-1.581117000	-0.065548000
Cl	-2.574267000	0.450995000	0.040161000
Cu	-0.436532000	0.431451000	0.018392000
Cl	1.728784000	0.722025000	0.006995000