Table1S. Vibrational Frequencies and Average Vibrational Energies at 298 K.

Species	E_{vib} eV[a]	Vibrational frequencies, cm^{-1} [b]
Imidazole	0.07 (0.01)	494, 632, 670, 704, 784, 840, 887, 925, 1061, 1085, 1135, 1149, 1268, 1355, 1422, 1490, 1545, 3200, 3204, 3231, 3580
Cu^+(imidazole)	0.11 (0.01)	132, 154, 366, 606, 633, 669, 740, 793, 855, 917, 975, 1084, 1116, 1142, 1204, 1273, 1343, 1444, 1527, 1571, 3242, 3247, 3260, 3559
Cu^+(imidazole)$_2$	0.25 (0.02)	32, 34(2), 124(2), 218(2), 243, 393, 594(2), 639(2), 664(2), 738, 739, 791(2), 849, 850, 919(2), 964, 965, 1078, 1080, 1111, 1112, 1139, 1141, 1189, 1193, 1269, 1271, 1347, 1348, 1443, 1444, 1522, 1524, 1568, 1569, 3238(2), 3245(2), 3257(2), 3570, 3571
Cu^+(imidazole)$_{2,1}$	0.40 (0.03)	15, 19, 20, 33, 38, 40, 88, 96, 119, 131, 147, 220, 223, 254, 397, 562, 589, 627, 638, 639, 650, 661, 670, 731, 736, 741, 789, 793, 796, 837, 845, 847, 900, 917, 919, 934, 964, 977, 1061, 1078(2), 1088, 1104, 1110, 1112, 1140, 1142, 1164, 1173, 1189, 1220, 1269, 1271, 1281, 1346, 1348, 1357, 1435, 1443, 1486, 1507, 1522, 1529, 1557, 1567, 1590, 2851, 3218, 3222, 3232, 3238, 3239, 3245, 3247, 3252, 3257, 3573, 3576
Cu^+(imidazole)$_{2,2}$	0.56 (0.04)	8, 13, 16, 22(2), 34, 38, 40, 41, 80, 85, 102, 106, 113, 125, 149, 150, 223, 226, 262, 400, 559, 560, 626, 627, 638(2), 650(2), 670(2), 729(2), 740, 741, 792(2), 796, 797, 835, 836, 845(2), 900(2), 917(2), 933, 934, 976, 977, 1054, 1055, 1073, 1074, 1086, 1088, 1102, 1103, 1111(2), 1141(2), 1163, 1164, 1172, 1175, 1217, 1218, 1271(2), 1279, 1281, 1347(2), 1357(2), 1434(2), 1486(2), 1506(2), 1527, 1529, 1557(2), 1589(2), 2889, 2899, 3217(2), 3222(2), 3231, 3232, 3239, 3240, 3245, 3246, 3252(2), 3576, 3577

[a]Uncertainties listed in parenthesis are determined as described in the text. [b]Vibrational frequencies scaled by 0.9804 obtained from a vibrational analysis of the geometry optimized structures for these species determined at the B3LYP/6-31G* level of theory.

Table 2S. Rotational Constants of Cu^+(imidazole)$_x$, x = 1 - 4 in cm^{-1}.

ML_x	Energized Molecule		Transition State		
	1-D[a]	2-D[b]	1-D[c]	2-D[c]	2-D[d]
Cu^+(imidazole)	0.32	0.046	0.16	0.32	0.0050
Cu^+(imidazole)$_2$	0.15	0.012	0.32, 0.33	0.05, 0.22	0.0056
Cu^+(imidazole)$_{2,1}$	0.06	0.004	0.16, 0.16	0.01, 0.32	0.0056
Cu^+(imidazole)$_{2,2}$	0.03	0.002	0.06, 0.16	0.04, 0.32	0.0084

[a]Active external. [b]Inactive external. [c]Rotational constants of the transition state treated as free internal rotors. [d]Two-dimensional rotational constant of the transition state at threshold, treated variationally and statistically.

Table 3S. Ground State B3LYP/6-31G* Optimized Geometries of Imidazole, Imidazole Dimer and $Cu^{+}(imidazole)_x$, x = 1-4.

	$(imidazole)_2$		(imidazole)		$Cu^{+}(imidazole)_2$
	x, y, z		x, y, z		x, y, z
N	-3.653291,-0.064024,-0.66840	N	-0.991987, -0.000128, -0.726098	N	1.824122, -0.002006, -0.012734
C	-3.651097,-0.071463,0.709017	C	-0.973356, 0.000044, 0.649914	C	2.623966, 0.797435, 0.792578
C	-2.364560,-0.072572,1.192906	C	0.031360, -0.000024, 1.112792	C	3.935739, 0.517197, 0.539671
N	-1.55295,-0.066708,0.080194	N	1.102832, 0.000029, -0.016252	N	3.927880, -0.463324, -0.430571
H	-0.526510,-0.063151,0.069692	H	2.106968, 0.000050, -0.040136	H	4.743019, -0.897432, -0.843743
H	-4.575541,-0.075497,1.271805	H	0,0.729158,-0.000039, 2.103357	H	2.204304, 1.507368, 1.488115
H	-1.960628,-0.078985,2.194604	H	3.155987, 1.280414, 0.000020	H	4.850339, 0.914771, 0.950440
C	-2.377435,-0.061375,-1.005063	C	0.266652, 0.000069, -1.093378	C	2.648462, -0.753020, -0.740875
H	-1.995084,-0.057086,-2.017687	H	0.629609, 0.000090, -2.106980	H	2.358884,-1.489692, -1.474559
C	2.172585,1.085523,-0.092879		Cu^{+}(imidazole)	Cu	0.000000, -0.000449, -0.038864
			x, y, z		
N	3.498639,0.781999,-0.156931	N	0.117285, -0.005059, -0.000017	C	-2.624133, -0.794061, 0.795633
C	3.613888,-0.592753,-0.103234	C	0.929254, 1.123243, 0.000018	C	-3.935838, -0.514162, 0.542010
C	2.328244,-1.057623,-0.009099	C	2.232842, 0.722264, 0.000015	N	-3.927779, 0.462287, -0.432331
N	1.437539,-0.004692,-0.003484	N	2.204282, -0.656909, -0.000049	C	-2.648308, 0.750027, -0.744236
H	1.801263,2.100717,-0.115342	H	3.012683, -1.267224, -0.000105	N	-1.824127, 0.001626, -0.013243
H	4.25894191.442488,-0.230576	H	0.526467, 2.123905, 0.000031	H	-2.204626, -1.501406, 1.493893
H	4.570261,-1.091448,-0.136629	H	3.155987, 1.280414, 0.000020	H	-4.850519, -0.909615, 0.954644
H	1.98800,-2.081468,0.054605	C	0.924935, -1.068735, 0.000064	H	-2.358579, 1.483412, -1.481146
		H	0.621439, -2.104368, 0.000107	H	-4.742819, 0.895034, -0.847121
		Cu	-1.658267, -0.002054, -0.000006		

	$Cu^{+}(imidazole)_{1,1}$		$Cu^{+}(imidazole)_{2,1}$		$Cu^{+}(imidazole)_3$
	x, y, z		x, y, z		x, y, z
N	-2.113183, 0.175981, 0.003175	N	0.293149, 0.723330, -0.039381	N	1.680455, -1.059794, -0.023874
C	-1.872260, 1.518338, -0.127890	C	-0.161968, 2.023020, -0.206467	C	2.798506, -0.635681, -0.725665
C	-0.520618, 1.733652, 0.125328	C	-1.528904, 2.014763, -0.200833	C	3.855560, -1.457952, -0.451651
N	0.060738, 0.492535, -0.001389	N	-1.910491, 0.703829, -0.028448	N	3.371698, -2.397361, 0.434013
H	1.107443, 0.288224, -0.031122	H	-2.899614, 0.344582, 0.017303	H	3.898544, -3.156780, 0.843705
H	-2.669934, -2.259867, 0.208375	H	0.516160, 2.854939, -0.318184	H	2.763793, 0.230040, -1.369385
H	0.067871, 2.634560, 0.203083	H	-2.249604, 2.810873, -0.303648	H	4.878226, -1.462215, -0.794891
C	-0.913232, -0.420475, -0.072106	H	-0.799171, -0.041873, 0.064261	C	2.064871, -2.127811, 0.664956
H	-0.741035, -1.480943, -0.174295	H	-0.805054, -1.112513, 0.201719	H	1.440112, -2.718139, 1.318139
Cu	-3.702408, -0.598814, -0.036237	Cu	2.036173, 0.201566, 0.0158161	Cu	-0.026422, -0.184691, -0.027836
C	3.623742, -0.007383, -1.056187	C	4.548650 -0.639059, -1.079055	C	1.114545, 2.509895, 0.585080
N	4.887689, -0.273787, -0.648543	C	5.820092, -0.937433, -0.681186	C	0.881955, 3.842942, 0.389439
C	4.858186, -0.474942, 0.719578	N	5.832915, -0.765271, 0.687461	N	-0.291931, 3.908756, -0.331794
C	3.547222, -0.317635, 1.080754	C	4.603591, -0.376326, 1.083861	C	-0.726375, 2.644387, -0.546113
N	2.784471, -0.026626, -0.033964	N	3.793562, -0.288494, 0.031383	N	0.105467, 1.764903, -0.002837
H	3.367716, 0.191193, -2.087180	H	4.128759, -0.650528, -2.072721	H	1.935939, 2.034843, 1.099827
H	5.707386, -0.315382, -1.234905	H	6.694131, -1.248021, -1.231453	H	1.425003, 4.725944, 0.688179
H	5.746292, -0.703586, 1.287842	H	4.338593, -0.171313, 2.109734	H	-1.633358, 2.408187, -1.082514
H	3.107848, -0.393165, 2.064849	H	6.628038, -0.904214, 1.296947	H	-0.748653, 4.752830, -0.650074
		C	-5.389262, -0.333138, 1.077340	C	-2.349048, -1.855901, -0.722294
		N	-6.602461, -0.800622, 0.688189	N	-3.662662, -1.999867, -0.424645
		C	0.688189, -1.024272, -0.672084	C	-3.991537, -1.067896, 0.536517
		C	-5.285438, -5.285438, -1.050835	C	-2.838284, -0.377650, 0.785832

N	-4.565988, -0.244946, 0.047205	N	-1.813544, -0.875392, -0.004739
H	-5.157815, -0.075039, 2.101046	H	-1.829809, -2.470151, -1.442446
H	-7.400596, -0.954176, 1.288989	H	-4.987412, -0.985928, 0.942991
H	-7.401103, -1.399219, -1.224935	H	-2.673571, 0.438977, 1.472296
H	-4.847893, -0.703013, -2.03833	H	-4.290115, -2.676280, -0.838043

Table 3S. (continued) Ground State B3LYP/6-31G* Optimized Geometries of Imidazole, Imidazole Dimer and $Cu^{+}(imidazole)_x$, x = 1-4.

	$Cu^{+}(imidazole)_{2,2}$		$Cu^{+}(imidazole)_{3,1}$		$Cu^{+}(imidazole)_4$
	x, y, z		x, y, z		x, y, z
N	-1.754246,-0.821646,-0.486770	N	-1.754246,-0.821646,-0.486770	N	1.309326, -1.089552, 1.063716
C	-2.329804, -1.639668, -1.447141	C	-0.621620, -1.587736, -1.173618	C	2.471866, -1.654384, 0.566744
C	-3.669601, -1.374084, -1.507938	C	-1.985844, -1.700920, -1.149499	C	3.131319, -2.324116, 1.562088
N	-3.913430, -0.387577, -0.579872	N	-2.446119, -0.632004, -0.416390	N	2.353498, -2.162486, 2.688830
H	-4.845981, 0.045182, -0.363572	H	-3.444228, -0.411617, -0.200664	H	2.554774, -2.527851, 3.609442
H	-1.747080, -2.348019, -2.014215	H	0.107700, -2.231398, -1.642152	H	2.757583, -1.526468, -0.466694
H	-4.455657, -1.792944, -2.116531	H	-2.654933, -2.429377, -1.580728	H	4.054704, -2.882092, 1.574577
C	-2.748422, -0.080387, 0.012485	C	-1.374756, 0.087047, -0.027412	C	1.272680, -1.414925, 2.346647
H	-2.647730, 0.665365, 0.786300	H	-1.446523, 0.991089, 0.558623	H	0.500050, -1.133511, 3.046804
Cu	0.003325, -0.798781, -0.011047	Cu	1.556761, 0.108343, -0.156397	Cu	-0.026867, -0.013434, 0.002894
C	2.310424, -1.595852, -1.487080	C	2.436528, -2.625442, 0.658675	C	2.361450, 1.687918, -0.783165
C	3.654395, -1.351516, 1.544436	C	3.526257, -3.451181, 0.678340	C	2.852211, 2.472828, -1.791321
N	3.925008, -0.430282, 0.558527	N	4.556625, -2.712217, 0.134656	N	1.915836, 2.399542, -2.800753
C	2.771147, -0.139001, -0.062956	C	4.071236, -1.489489, -0.189573	C	0.910631, 1.589466, -2.379995
N	1.758810, -0.829064, 0.471873	N	2.783614, -1.400364, 0.114162	N	1.146404, 1.139593, -1.157068
H	1.709373, -2.257085, 2.091936	H	1.427958, -2.825654, 0.987536	H	2.797698, 1.472763, 0.180667
H	4.426503, -1.743417, 2.187857	H	3.66250, -4.465939, 1.018297	H	3.753207, 3.059228, -1.882781
H	2.691045, 0.560051, -0.881467	H	4.672095, -0.70691, -0.628700	H	0.044925, 1.356200, -2.982069
H	4.865970, -0.023053, 0.328496	H	5.506960, -3.027704, -0.004369	H	1.967901, 2.863465, -3.697109
C	-7.080042, 1.728663, -0.563713	C	2.286777, 2.894410, -0.744641	C	-1.028054, -2.561704, -1.216045
N	-8.297578, 1.927822, 0.002695	N	3.090288, 3.887560, -0.291488	N	-2.065097, -3.108636, -1.901202
C	-8.449201, 1.003882, 1.015723	C	3.750820, 3.429195, 0.828487	C	-3.014484, -2.126876, -2.089265
C	-7.290944, 0.273445, 1.014785	C	3.314624, 2.146396, 1.010461	C	-2.498026, -1.005462, -1.497889
N	-6.442726, 0.732975, 0.026413	N	2.398208, 1.817664, 0.023437	N	-1.256354, -1.284085, -0.953626
H	-6.709499, 2.321794, -1.387779	H	1.646155, 2.991984, -1.608032	H	-0.145671, -3.114817, -0.929921
H	-8.973252, 2.627627, -0.271391	H	4.449112, 4.041995, 1.376723	H	-3.939902, -2.312643, -2.611986
H	-9.340104, 0.954987, 1.622296	H	3.594115, 1.438530, 1.775986	H	-2.933562, -0.020204, -1.422549
H	-7.016175, -0.549843, 1.658359	H	3.184176, 4.805042, -0.705081	H	-2.128646, -4.067146, -2.215229
C	6.979679, 1.834943, 0.506517	C	-5.924379, -0.376027, 1.170050	C	-2.061374, 3.042005, 2.041803
C	8.233715, 2.068135, 0.008235	N	-7.192332, 0.096168, 1.050372	C	-1.031300, 2.533333, 1.298704
N	8.471066, 1.036975, -0.876763	C	-7.268258, 0.806452, -0.129782	N	-1.242109, 1.187898, 1.053585
C	7.376957, 0.233406, -0.882949	C	-6.015896, 0.728516, -0.678825	C	-2.389531, 0.88962, 1.644949
N	6.452895, 0.688639, -0.055440	N	-5.184333, -0.010738, 0.138831	N	-2.918574, 1.982639, 2.253752
H	6.426459, 2.416193, 1.230100	H	-5.595406, -0.971002, 2.010373	H	-3.787619, 2.012919, 2.768542
H	8.958469, 2.845292, 0.194893	H	-8.178691, 1.284276, -0.456748	H	-2.260276, 4.029619, 2.427959
H	9.310856, 0.901550, -1.422558	H	-5.663028, 1.154335, -1.607142	H	-0.156400, 3.039927, 0.919877
H	7.301972, -0.654734, -1.494397	H	-7.945836, -0.049513, 1.707774	H	-2.864472, -0.080412, 1.646384