

# Supporting information for: The Barrier To Linearity and Anharmonic Force Field of the Ketenyl Radical

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Table 1: Quadratic force constants and harmonic vibrational frequencies ( $\text{cm}^{-1}$ ) for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

$ij$	ROHF	CCSD	CCSD(T)
11	6.2619	6.0834	6.0614
21	-0.1174	-0.1164	-0.1174
22	10.0587	9.6643	9.6641
31	-0.0507	-0.0399	-0.0419
32	1.7364	1.6543	1.4855
33	14.5224	14.3983	14.3633
41	0.1879	0.1621	0.1599
42	0.8579	0.7366	0.7086
43	-0.2987	-0.2653	-0.2410
44	0.2009	0.2127	0.2225
51	0.0326	0.0385	0.0394
52	0.4872	0.4418	0.4374
53	0.1102	0.1329	0.1362
54	-0.0240	-0.0453	-0.0513
55	0.8646	0.7188	0.6803
66	0.6569	0.5141	0.4841
$\omega_1$	3394	3345	3339
$\omega_2$	2076	2054	2066
$\omega_3$	1264	1243	1235
$\omega_4$	636	576	563
$\omega_5$	575	508	511
$\omega_6$	424	486	493

Table 2: Cubic force constants for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

<i>ijk</i>	ROHF	CCSD	CCSD(T)	<i>ijk</i>	ROHF	CCSD	CCSD(T)
111	-34.848	-34.625	-34.628	511	-0.003	0.007	0.012
211	-0.005	0.026	0.034	521	0.015	0.040	0.040
221	-0.508	-0.484	-0.471	522	0.283	0.151	0.093
222	-61.961	-58.456	-58.161	531	-0.064	-0.059	-0.058
311	0.144	0.114	0.089	532	-0.389	-0.397	-0.401
321	0.110	0.085	0.067	533	-0.112	-0.061	-0.085
322	-2.710	-4.308	-4.266	541	-0.027	-0.028	-0.028
331	-0.116	-0.027	-0.005	542	0.090	0.037	0.020
332	-2.065	0.059	-0.200	543	0.039	0.017	0.007
333	-108.169	-107.165	-106.393	544	-0.383	-0.323	-0.305
411	0.048	0.009	0.010	551	-0.060	-0.066	-0.070
421	-0.055	-0.078	-0.102	552	-1.103	-1.004	-1.009
422	0.278	-0.004	-0.113	553	-1.110	-1.170	-1.194
431	-0.051	-0.047	-0.044	554	-0.007	-0.029	-0.029
432	0.102	0.066	0.063	555	-0.734	-0.660	-0.645
433	0.245	0.164	0.214	661	-0.053	-0.072	-0.078
441	-0.325	-0.291	-0.278	662	-0.932	-0.845	-0.837
442	-0.253	-0.326	-0.306	663	-0.979	-1.034	-1.033
443	-0.101	-0.027	-0.010	664	0.056	0.075	0.084
444	-0.497	-0.468	-0.491	665	-0.390	-0.388	-0.370

Table 3: Quartic force constants for the HCCO radical. All force constant units are consistent with energies in aJ, distances in Å, and angles in radians.

<i>ijkl</i>	ROHF	CCSD	CCSD(T)	<i>ijkl</i>	ROHF	CCSD	CCSD(T)
2111	19.82	5.28	-1.49	5333	9.97	3.40	0.49
2211	-29.91	-10.68	-1.29	5411	-3.50	-1.02	0.07
2221	20.15	5.92	-1.21	5421	26.98	9.05	0.05
2222	210.56	248.74	271.93	5422	-2.32	-0.30	0.95
3111	21.29	6.34	0.22	5431	26.68	7.92	0.11
3211	-14.14	-4.30	0.09	5432	26.61	8.55	-0.33
3221	-14.05	-3.80	0.42	5433	-3.50	-1.00	0.04
3222	41.14	28.15	16.54	5441	-1.73	-0.53	0.01
3311	-28.73	-8.58	-0.42	5442	-2.58	-1.34	-0.64
3321	-14.60	-5.15	-0.66	5443	-1.47	-0.22	0.35
3322	-32.36	-21.65	-8.98	5444	1.44	0.61	0.15
3331	21.86	7.17	1.02	5511	-7.19	-2.18	-0.14
3332	20.80	20.36	11.87	5521	-3.59	-1.16	0.02
3333	566.70	588.17	604.05	5522	-7.73	-2.34	0.55
4111	10.21	2.74	-0.41	5531	-3.49	-0.89	0.05
4211	-6.84	-2.17	0.20	5532	-1.14	1.10	2.08
4221	-7.28	-2.16	0.22	5533	-7.20	-1.85	0.51
4222	12.94	5.80	1.48	5541	-1.80	-0.56	-0.03
4311	-7.22	-2.21	-0.08	5542	-2.06	-1.06	-0.43
4321	53.42	16.77	-0.10	5543	-2.17	-0.87	-0.28
4322	-7.27	-3.36	-1.29	5544	-1.85	-0.59	0.02
4331	-7.05	-2.05	0.01	5551	2.83	0.92	0.17
4332	-8.15	-2.33	0.34	5552	4.41	2.45	1.36
4333	11.25	2.65	-0.62	5553	3.77	1.92	1.10
4411	-7.01	-2.03	0.09	5554	1.33	0.39	-0.07
4421	-3.04	-0.77	0.38	5555	2.99	4.11	4.75
4422	-5.91	-1.95	0.52	6611	-7.15	-2.13	-0.15
4431	-3.66	-1.08	-0.01	6621	-3.69	-1.38	-0.23
4432	-4.32	-1.49	-0.13	6622	-9.84	-4.40	-1.51
4433	-6.85	-2.06	-0.13	6631	-3.49	-0.96	0.04
4441	3.13	1.30	0.48	6632	-1.59	0.47	1.59
4442	0.66	-0.40	-1.19	6633	-7.11	-1.84	0.51
4443	3.83	1.65	0.73	6641	-1.77	-0.51	0.01
4444	-2.14	-0.68	0.04	6642	-2.04	-0.81	-0.11
5111	10.63	3.08	0.02	6643	-1.96	-0.72	-0.17
5211	-7.03	-2.21	0.13	6644	-1.69	-0.47	0.08
5221	-7.10	-2.27	0.08	6651	-1.72	-0.52	-0.03
5222	10.39	3.89	-0.19	6652	-1.27	-0.21	0.46
5311	-7.21	-2.21	-0.10	6653	-1.21	0.01	0.59
5321	53.36	16.64	0.04	6654	-1.10	-0.35	-0.01
5322	-5.23	-0.89	1.06	6655	-0.92	0.01	0.59
5331	-7.04	-1.99	-0.02	6666	1.45	3.17	3.80