

SUPPLEMENTAL INFORMATION

for

High-resolution infrared spectroscopy of jet cooled cyclobutyl in the α -CH stretch region:

Large-amplitude puckering dynamics in a 4-membered ring radical

Ya-Chu Chan^{1,2} and David J. Nesbitt^{1,2,3}

¹ JILA, University of Colorado Boulder and National Institute of Standards and Technology,

Boulder, Colorado 80309

² Department of Chemistry, University of Colorado Boulder, Boulder, Colorado 80309

³ Department of Physics, University of Colorado Boulder, Boulder, Colorado 80309

TABLE S1. Observed and calculated transition frequencies in cm^{-1} of cyclobutyl radical $\alpha\text{-CH}$ stretch rovibrational band.

N'	K_a'	K_c'	N''	K_a''	K_c''	Obs.	Calc.	Obs. - Calc.
1	1	1	0	0	0	3069.3987	3069.3971	0.0016
2	2	1	1	1	0	3070.1890	3070.1879	0.0011
3	3	1	2	2	0	3070.9923	3070.9922	0.0001
4	4	1	3	3	0	3071.8060	3071.8037	0.0023
6	6	1	5	5	0	3073.4218	3073.4197	0.0021
7	7	1	6	6	0	3074.2179	3074.2173	0.0006
2	0	2	1	1	1	3069.7805	3069.7843	-0.0038
3	1	2	2	2	1	3070.4885	3070.4894	-0.0009
4	2	2	3	3	1	3071.1540	3071.1535	0.0005
4	3	2	3	2	1	3071.4202	3071.4180	0.0022
5	4	2	4	3	1	3072.2388	3072.2384	0.0004
6	5	2	5	4	1	3073.0670	3073.0702	-0.0032
7	6	2	6	5	1	3073.9058	3073.9075	-0.0017
3	0	3	2	1	2	3070.2244	3070.2274	-0.0030
3	1	3	2	0	2	3070.2291	3070.2327	-0.0036
4	1	3	3	2	2	3070.9660	3070.9721	-0.0061
4	2	3	3	1	2	3070.9923	3070.9988	-0.0065
5	2	3	4	3	2	3071.7050	3071.7016	0.0034
6	3	3	5	4	2	3072.4075	3072.4060	0.0015
7	5	3	6	4	2	3073.4144	3073.4077	0.0067
4	0	4	3	1	3	3070.6489	3070.6546	-0.0057
4	1	4	3	0	3	3070.6586	3070.6551	0.0035
5	1	4	4	2	3	3071.4067	3071.4070	-0.0003
5	2	4	4	1	3	3071.4101	3071.4104	-0.0003
6	2	4	5	3	3	3072.1538	3072.1560	-0.0022
6	3	4	5	2	3	3072.1674	3072.1697	-0.0023
7	3	4	6	4	3	3072.8950	3072.8982	-0.0032
8	4	4	7	5	3	3073.6228	3073.6276	-0.0048
5	0	5	4	1	4	3071.0758	3071.0797	-0.0039
5	1	5	4	0	4	3071.0758	3071.0797	-0.0039
6	1	5	5	2	4	3071.8162	3071.8321	-0.0159
6	2	5	5	1	4	3071.8357	3071.8324	0.0033
6	0	6	5	1	5	3071.5034	3071.5045	-0.0011
6	1	6	5	0	5	3071.5034	3071.5045	-0.0011
7	1	6	6	2	5	3072.2709	3072.2560	0.0150
7	2	6	6	1	5	3072.2709	3072.2560	0.0150
8	2	6	7	3	5	3073.0135	3073.0067	0.0068
8	3	6	7	2	5	3073.0135	3073.0069	0.0066

9	3	6	8	4	5	3073.7565	3073.7570	-0.0005
9	4	6	8	3	5	3073.7565	3073.7577	-0.0012
7	0	7	6	1	6	3071.9335	3071.9293	0.0042
7	1	7	6	0	6	3071.9335	3071.9293	0.0042
8	1	7	7	2	6	3072.6770	3072.6797	-0.0027
8	2	7	7	1	6	3072.6770	3072.6797	-0.0027
9	2	7	8	3	6	3073.4144	3073.4293	-0.0149
9	3	7	8	2	6	3073.4418	3073.4293	0.0125
8	0	8	7	1	7	3072.3637	3072.3541	0.0096
8	1	8	7	0	7	3072.3637	3072.3541	0.0096
9	1	8	8	2	7	3073.1048	3073.1034	0.0014
9	2	8	8	1	7	3073.1048	3073.1034	0.0014
9	0	9	8	1	8	3072.7370	3072.7787	-0.0417
9	1	9	8	0	8	3072.8014	3072.7787	0.0227
10	1	9	9	2	8	3073.4742	3073.5271	-0.0529
10	2	9	9	1	8	3073.5370	3073.5271	0.0099
10	0	10	9	1	9	3073.1831	3073.2034	-0.0203
10	1	10	9	0	9	3073.2414	3073.2034	0.0380
11	0	11	10	1	10	3073.6228	3073.6280	-0.0052
11	1	11	10	0	10	3073.6228	3073.6280	-0.0052
12	0	12	11	1	11	3074.0607	3074.0525	0.0082
12	1	12	11	0	11	3074.0607	3074.0525	0.0082
2	2	0	1	1	1	3070.4609	3070.4606	0.0003
3	3	0	2	2	1	3071.2032	3071.2032	0.0000
4	4	0	3	3	1	3071.9503	3071.9500	0.0003
5	5	0	4	4	1	3072.7059	3072.7062	-0.0003
6	6	0	5	5	1	3073.4742	3073.4722	0.0020
7	7	0	6	6	1	3074.2466	3074.2456	0.0010
4	3	1	3	2	2	3072.1674	3072.1694	-0.0020
5	4	1	4	3	2	3072.8721	3072.8643	0.0078
6	5	1	5	4	2	3073.5527	3073.5595	-0.0068
1	0	1	1	1	0	3068.6043	3068.6042	0.0001
2	1	1	2	2	0	3068.5649	3068.5644	0.0005
3	2	1	3	3	0	3068.4972	3068.4965	0.0007
4	3	1	4	4	0	3068.3930	3068.3944	-0.0014
5	4	1	5	5	0	3068.2643	3068.2572	0.0071
6	5	1	6	6	0	3068.0838	3068.0914	-0.0076
2	0	2	2	1	1	3068.3267	3068.3305	-0.0038
3	1	2	3	2	1	3068.3545	3068.3550	-0.0005
3	2	2	3	3	1	3068.1857	3068.1810	0.0047
4	2	2	4	3	1	3068.3674	3068.3664	0.0010
5	3	2	5	4	1	3068.3566	3068.3530	0.0036
5	4	2	5	5	1	3068.0137	3068.0123	0.0014

7	5	2	7	6	1	3068.2327	3068.2192	0.0135
3	0	3	3	1	2	3067.9681	3067.9713	-0.0032
4	1	3	4	2	2	3067.9897	3067.9956	-0.0059
4	2	3	4	3	2	3067.9262	3067.9318	-0.0056
6	3	3	6	4	2	3068.0801	3068.0784	0.0017
7	5	3	7	6	2	3067.8063	3067.7987	0.0076
5	1	4	5	2	3	3067.6312	3067.6322	-0.0010
6	2	4	6	3	3	3067.6446	3067.6476	-0.0030
6	3	4	6	4	3	3067.6118	3067.6142	-0.0024
7	3	4	7	4	3	3067.6754	3067.6780	-0.0026
8	4	4	8	5	3	3067.7190	3067.7252	-0.0062
5	0	5	5	1	4	3067.2869	3067.2913	-0.0044
6	1	5	6	2	4	3067.2737	3067.2904	-0.0167
6	2	5	6	3	4	3067.2921	3067.2889	0.0032
7	1	6	7	2	5	3066.9696	3066.9542	0.0154
7	2	6	7	3	5	3066.9696	3066.9541	0.0155
1	1	0	1	0	1	3068.9716	3068.9710	0.0006
2	2	0	2	1	1	3069.0073	3069.0068	0.0005
3	3	0	3	2	1	3069.0691	3069.0688	0.0003
4	4	0	4	3	1	3069.1633	3069.1629	0.0004
5	5	0	5	4	1	3069.2897	3069.2901	-0.0004
6	6	0	6	5	1	3069.4460	3069.4439	0.0021
7	7	0	7	6	1	3069.6135	3069.6125	0.0010
2	1	1	2	0	2	3069.2431	3069.2426	0.0005
2	2	1	2	1	2	3069.3378	3069.3366	0.0012
3	2	1	3	1	2	3069.2135	3069.2122	0.0013
3	3	1	3	2	2	3069.3861	3069.3859	0.0002
4	3	1	4	2	2	3069.1919	3069.1930	-0.0011
4	4	1	4	3	2	3069.4540	3069.4524	0.0016
5	4	1	5	3	2	3069.2039	3069.1966	0.0073
5	5	1	5	4	2	3069.5374	3069.5361	0.0013
6	6	1	6	5	2	3069.6377	3069.6356	0.0021
7	6	1	7	5	2	3069.2983	3069.3050	-0.0067
7	7	1	7	6	2	3069.7498	3069.7489	0.0009
3	2	2	3	1	3	3069.6274	3069.6227	0.0047
5	3	2	5	2	3	3069.5224	3069.5190	0.0034
5	4	2	5	3	3	3069.6501	3069.6492	0.0008
6	5	2	6	4	3	3069.6771	3069.6807	-0.0036
7	6	2	7	5	3	3069.7262	3069.7280	-0.0018
4	2	3	4	1	4	3069.9377	3069.9449	-0.0072
5	1	4	5	0	5	3070.2744	3070.2748	-0.0004
6	2	4	6	1	5	3070.2622	3070.2637	-0.0015
6	3	4	6	2	5	3070.2621	3070.2652	-0.0031

9	3	6	9	2	7	3070.9112	3070.9121	-0.0009
9	4	6	9	3	7	3070.9112	3070.9122	-0.0010
2	2	1	3	3	0	3066.3662	3066.3648	0.0014
3	3	1	4	4	0	3065.6110	3065.6108	0.0002
4	4	1	5	5	0	3064.8467	3064.8454	0.0013
5	5	1	6	6	0	3064.0693	3064.0680	0.0013
6	6	1	7	7	0	3063.2828	3063.2810	0.0018
7	7	1	8	8	0	3062.4885	3062.4876	0.0009
4	2	3	5	3	2	3064.2586	3064.2642	-0.0056
1	1	0	2	2	1	3067.3855	3067.3852	0.0003
2	2	0	3	3	1	3066.5761	3066.5757	0.0004
3	3	0	4	4	1	3065.7575	3065.7571	0.0004
4	4	0	5	5	1	3064.9367	3064.9368	-0.0001
5	5	0	6	6	1	3064.1197	3064.1204	-0.0007
6	6	0	7	7	1	3063.3115	3063.3092	0.0023
1	0	1	2	1	2	3067.7530	3067.7529	0.0001
1	1	1	2	0	2	3067.7927	3067.7907	0.0020
2	1	1	3	2	2	3066.9583	3066.9581	0.0002
2	2	1	3	1	2	3067.0823	3067.0806	0.0017
3	3	1	4	2	2	3066.4091	3066.4094	-0.0003
4	3	1	5	4	2	3065.3140	3065.3158	-0.0018
5	4	1	6	5	2	3064.4818	3064.4732	0.0086
6	5	1	7	6	2	3063.6158	3063.6230	-0.0072
2	0	2	3	1	3	3067.3380	3067.3412	-0.0032
3	1	2	4	2	3	3066.5675	3066.5680	-0.0005
4	3	2	5	2	3	3065.8581	3065.8562	0.0019
5	3	2	6	4	3	3064.9667	3064.9635	0.0032
5	4	2	6	3	3	3065.1420	3065.1408	0.0012
7	5	2	8	6	3	3063.2828	3063.2690	0.0138
3	0	3	4	1	4	3066.9144	3066.9174	-0.0030
3	1	3	4	0	4	3066.9144	3066.9179	-0.0035
3	2	2	4	1	3	3066.5994	3066.5948	0.0046
4	1	3	5	2	4	3066.1467	3066.1531	-0.0064
4	2	3	5	1	4	3066.1512	3066.1566	-0.0054
5	2	3	6	3	4	3065.3860	3065.3828	0.0032
6	3	3	7	4	4	3064.6027	3064.6009	0.0018
4	0	4	5	1	5	3066.4855	3066.4913	-0.0058
4	1	4	5	0	5	3066.4954	3066.4914	0.0040
5	1	4	6	2	5	3065.7277	3065.7277	0.0000
5	2	4	6	1	5	3065.7277	3065.7280	-0.0003
6	2	4	7	3	5	3064.9600	3064.9618	-0.0018
6	3	4	7	2	5	3064.9600	3064.9635	-0.0035
7	3	4	8	4	5	3064.1894	3064.1921	-0.0027

8	4	4	9	5	5	3063.4093	3063.4155	-0.0062
5	0	5	6	1	6	3066.0610	3066.0650	-0.0040
5	1	5	6	0	6	3066.0610	3066.0650	-0.0040
6	1	5	7	2	6	3065.2848	3065.3006	-0.0157
6	2	5	7	1	6	3065.3043	3065.3006	0.0037
6	0	6	7	1	7	3065.6374	3065.6386	-0.0012
6	1	6	7	0	7	3065.6374	3065.6386	-0.0012
7	1	6	8	2	7	3064.8881	3064.8732	0.0148
7	2	6	8	1	7	3064.8881	3064.8732	0.0148
8	2	6	9	3	7	3064.1139	3064.1066	0.0073
8	3	6	9	2	7	3064.1134	3064.1066	0.0068
9	3	6	10	4	7	3063.3377	3063.3385	-0.0008
9	4	6	10	3	7	3063.3377	3063.3385	-0.0008
7	0	7	8	1	8	3065.2167	3065.2121	0.0046
7	1	7	8	0	8	3065.2167	3065.2121	0.0046
8	1	7	9	2	8	3064.4433	3064.4458	-0.0024
8	2	7	9	1	8	3064.4433	3064.4458	-0.0024
9	2	7	10	3	8	3063.6623	3063.6782	-0.0159
9	3	7	10	2	8	3063.6905	3063.6782	0.0122
8	0	8	9	1	9	3064.7954	3064.7855	0.0099
8	1	8	9	0	9	3064.7954	3064.7855	0.0099
9	1	8	10	2	9	3064.0193	3064.0182	0.0011
9	2	8	10	1	9	3064.0193	3064.0182	0.0011
9	0	9	10	1	10	3064.3171	3064.3590	-0.0419
9	1	9	10	0	10	3064.3815	3064.3590	0.0225
10	1	9	11	2	10	3063.5359	3063.5906	-0.0547
10	2	9	11	1	10	3063.6007	3063.5906	0.0100
10	0	10	11	1	11	3063.9119	3063.9323	-0.0204
10	1	10	11	0	11	3063.9706	3063.9323	0.0383
11	0	11	12	1	12	3063.5005	3063.5056	-0.0051
11	1	11	12	0	12	3063.5006	3063.5056	-0.0050
12	0	12	13	1	13	3063.0874	3063.0788	0.0086
12	1	12	13	0	13	3063.0874	3063.0788	0.0086

TABLE S2. Four-line combination difference (4-line CD) analysis (in cm^{-1}) confirming observed transitions are from the same lower state, which is assigned to the rotational levels of the vibrational ground state.

P or R branch transition							Q branch transition							2-line CD	4-line CD
N'	K_a'	K_c'	N''	K_a''	K_c''	Position	N'	K_a'	K_c'	N''	K_a''	K_c''	Position		
2	0	2	1	1	1	3069.7805	2	0	2	2	1	1	3068.3267	1.4538	0.0002
2	2	0	1	1	1	3070.4609	2	2	0	2	1	1	3069.0073	1.4536	
3	1	2	2	2	1	3070.4885	3	1	2	3	2	1	3068.3545	2.1340	0.0001
3	3	0	2	2	1	3071.2032	3	3	0	3	2	1	3069.0691	2.1341	
4	4	0	3	3	1	3071.9503	4	4	0	4	3	1	3069.1633	2.7870	0.0004
4	2	2	3	3	1	3071.1540	4	2	2	4	3	1	3068.3674	2.7866	
3	0	3	2	1	2	3070.2244	3	0	3	3	1	2	3067.9681	2.2563	0.0008
2	2	1	2	1	2	3069.3378	2	2	1	3	1	2	3067.0823	2.2555	
4	1	3	3	2	2	3070.9660	4	1	3	4	2	2	3067.9897	2.9763	0.0008
4	3	1	3	2	2	3072.1674	4	3	1	4	2	2	3069.1919	2.9755	
5	4	1	4	3	2	3072.8721	5	4	1	5	3	2	3069.2039	3.6682	0.0005
4	2	3	5	3	2	3064.2586	4	2	3	4	3	2	3067.9262	3.6677	
6	3	4	5	2	3	3072.1674	6	3	4	6	4	3	3067.6118	4.5557	0.0001
5	3	2	6	4	3	3064.9667	5	3	2	5	2	3	3069.5224	4.5556	
5	0	5	4	1	4	3071.0758	5	0	5	5	1	4	3067.2869	3.7890	0.0025
4	2	3	4	1	4	3069.9377	4	2	3	5	1	4	3066.1512	3.7865	
2	1	1	3	2	2	3066.9583	2	1	1	2	2	0	3068.5649	1.6066	0.0003
3	3	1	2	2	0	3070.9923	3	3	1	3	2	2	3069.3861	1.6063	
4	3	1	3	2	2	3072.1674	4	3	1	4	4	0	3068.3930	3.7745	0.0006
3	3	1	4	4	0	3065.6110	3	3	1	3	2	2	3069.3861	3.7751	
5	3	2	6	4	3	3064.9667	5	3	2	5	4	1	3068.3566	3.3899	0.0000
6	5	2	5	4	1	3073.0670	6	5	2	6	4	3	3069.6771	3.3899	

Fig. S1: Convergence in CCSD(T) puckering barrier in cyclobutyl radical as a function of basis set completeness. Note the rapid decrease in barrier height for both ANOn($n=0,1,2$) and correlation consistent Dunning-type PVnZ($n=2,3,4$) basis sets to extremely small values (a few cm^{-1}). Thus, complete vanishing of the puckering barrier for cyclobutyl radical should not be ruled out for even higher levels of ab initio theory.

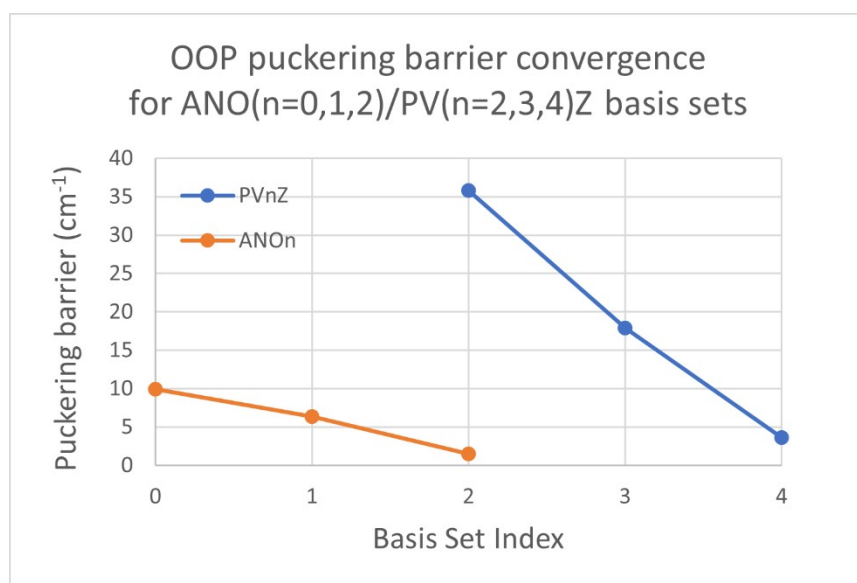


Fig. S2: Convergence in CCSD(T) puckering geometry in cyclobutyl radical as a function of basis set completeness. Note the rapid decrease in puckering angle for both ANOn($n=0,1,2$) and correlation consistent Dunning-type PVnZ($n=2,3,4$) basis sets to values on the order of 3-4 degrees. This suggests that a perfectly planar CCCC ring equilibrium geometry of cyclobutyl radical should not be ruled out for even higher levels of ab initio theory.

