Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

State-of-the-art computation of the rotational and IR spectrum of the methyl-cyclopropyl cation: Hints on its detection in space

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TABLE S.1 – Comparison of harmonic frequencies and intensities at different levels of theory

	CCSD(T)/cc-pVTZ		MP2/cc-pVTZ		MP2/cc-pVQZ		all-MP2/cc-pCVTZ		fc-MP2/cc-pCVTZ		MP2/cc-pVTZ	
	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)
A''	38.3668	0.9860	40.5392	1.1027	40.6632	1.0850	41.1380	1.1479	40.8675	1.1104	37.7591	0.9465
A''	354.9176	1.7176	357.6075	1.8818	357.1521	1.9109	359.7600	1.9476	358.3034	1.9008	356.0011	1.8569
A'	386.8880	4.8921	391.1872	4.9603	390.0342	4.6486	393.6595	5.0508	391.8668	4.9592	388.3658	4.5376
A'	765.0933	2.0505	776.9866	1.3357	778.3469	1.2899	780.3089	1.2923	777.1705	1.3223	776.5297	1.1780
A'	829.5600	56.9732	836.9964	53.2472	836.7363	50.6188	839.2958	52.6103	837.3697	53.0851	837.7903	50.7230
A''	975.0480	8.6587	978.5667	9.2123	978.4793	9.1047	980.7080	9.0517	978.5028	9.2379	973.8892	9.9513
A'	982.3970	38.3662	985.7416	38.4457	983.7857	38.4843	986.5945	38.9930	985.1721	38.4478	982.3195	38.4078
A''	1006.0527	0.4855	1011.9966	0.5348	1014.3483	0.4802	1016.4126	0.5046	1013.7207	0.5199	1012.2641	0.4984
A'	1045.5700	34.4862	1045.8524	37.0788	1045.1351	37.2752	1047.8296	38.1423	1045.9769	37.1994	1045.7466	35.9683
A''	1086.4373	18.7812	1089.2259	19.128	1089.8898	19.3223	1092.4608	19.7513	1089.7488	19.1419	1086.1580	18.1856
A''	1293.2634	3.6883	1304.7481	1.6789	1308.9066	1.6057	1310.1032	1.6960	1305.6819	1.7436	1303.9767	1.5994
A'	1394.8050	3.2979	1397.1531	4.8544	1397.1020	6.2323	1399.4404	6.5606	1397.6328	5.2335	1400.0131	3.2427
A'	1408.5549	110.0893	1420.8653	100.0788	1425.4832	99.8926	1427.1639	101.1235	1422.0309	100.6318	1418.7798	100.4685
A''	1460.6528	21.4803	1467.7627	21.6278	1466.6685	21.6614	1469.3394	22.2525	1467.8393	21.7800	1470.8579	21.0562
A'	1486.2475	9.5627	1494.4958	10.1934	1493.9949	10.1519	1496.8697	10.4828	1494.8453	10.2270	1497.5908	9.8933
A'	1751.8935	55.7420	1762.3327	58.1521	1766.4808	58.2793	1769.4649	59.3309	1762.4769	58.4558	1761.5727	57.9699
A'	3042.7842	22.8274	3075.9689	28.3954	3076.3894	30.1509	3081.3277	29.4237	3076.2373	28.5298	3070.6566	29.5696
A'	3128.3326	5.7316	3170.0991	9.3299	3171.7615	9.7405	3176.3024	9.8951	3170.8612	9.5156	3164.4049	9.2436
A''	3176.9922	3.8884	3221.8085	7.1368	3224.0798	7.4065	3228.4481	7.5268	3222.7281	7.1564	3215.7981	7.0773
A''	3254.2953	102.8518	3284.0981	116.4432	3286.2509	116.6693	3288.8794	117.3021	3283.4079	116.0795	3274.7671	116.1824
A'	3290.9049	49.1324	3320.5787	54.2952	3318.5053	54.2429	3321.2574	54.7131	3315.6248	54.0435	3309.4200	54.2369

TABLE S.2 – CBS, CV and AUG contributions to the "cheap" best-estimated harmonic frequencies and intensities

	CBS correction MP2/CBS – MP2/cc-pVTZ		CV correction all-MP2 – fc-MP2 (CVTZ)		AUG (MP2)correction aug-cc-pVTZ – cc-pVTZ		(T) contribution CCSD(T) – MP2 /cc-pVTZ	
	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)
A''	0.21449	-0.03062	0.2705	0.0375	-2.7801	-0.1562	-2.1724	-0.1167
A''	-0.78772	0.05034	1.4566	0.0468	-1.6064	-0.0249	-2.6899	-0.1642
A'	-1.99438	-0.53916	1.7927	0.0916	-2.8214	-0.4227	-4.2992	-0.0682
A'	2.35295	-0.07922	3.1384	-0.0300	-0.4569	-0.1577	-11.8933	0.7148
A'	-0.4499	-4.54642	1.9261	-0.4748	0.7939	-2.5242	-7.4364	3.7260
A''	-0.15118	-0.18612	2.2052	-0.1862	-4.6775	0.739	-3.5187	-0.5536
A'	-3.38318	0.06677	1.4224	0.5452	-3.4221	-0.0379	-3.3446	-0.0795
A''	4.06781	-0.09444	2.6919	-0.0153	0.2675	-0.0364	-5.9439	-0.0493
A'	-1.24074	0.33972	1.8527	0.9429	-0.1058	-1.1105	-0.2824	-2.5926
A''	1.14837	0.33609	2.7120	0.6094	-3.0679	-0.9424	-2.7886	-0.3468
A''	7.19308	-0.12662	4.4213	-0.0476	-0.7714	-0.0795	-11.4847	2.0094
A'	-0.08839	2.38339	1.8076	1.3271	2.8600	-1.6117	-2.3481	-1.5565
A'	7.98772	-0.32208	5.1330	0.4917	-2.0855	0.3897	-12.3104	10.0105
A''	-1.89267	0.05812	1.5001	0.4725	3.0952	-0.5716	-7.1099	-0.1475
A'	-0.86642	-0.07178	2.0244	0.2558	3.0950	-0.3001	-8.2483	-0.6307
A'	7.17509	0.22002	6.9880	0.8751	-0.7600	-0.1822	-10.4392	-2.4101
A'	0.72735	3.03654	5.0904	0.8939	-5.3123	1.1742	-33.1847	-5.5680
A'	2.87550	0.71023	5.4412	0.3795	-5.6942	-0.0863	-41.7665	-3.5983
A''	3.92874	0.46651	5.7200	0.3704	-6.0104	-0.0595	-44.8163	-3.2484
A''	3.72376	0.39109	5.4715	1.2226	-9.3310	-0.2608	-29.8028	-13.5914
A'	-3.58642	-0.09046	5.6326	0.6696	-11.1587	-0.0583	-29.6738	-5.1628

TABLE S.3 – Harmonic frequencies and intensities at the HF-SCF, MP2 and CCSD(T) level in conjuction with the same basis set (cc-pVTZ)

	HF/cc-pVTZ		MP2/cc-pVTZ		CCSD(T)/cc-pVTZ	
	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)	Freq (cm-1)	Inte (km/mol)
A''	32.1742	0.5012	40.5392	1.1027	38.3668	0.9860
A''	381.2289	1.9764	357.6075	1.8818	354.9176	1.7176
A'	423.0651	10.3877	391.1872	4.9603	386.8880	4.8921
A'	794.7168	0.3070	776.9866	1.3357	765.0933	2.0505
A'	927.5394	30.0082	836.9964	53.2472	829.5600	56.9732
A''	1069.0073	0.0058	978.5667	9.2123	975.0480	8.6587
A'	1060.7338	25.4039	985.7416	38.4457	982.3970	38.3662
A''	1118.9605	0.0314	1011.9966	0.5348	1006.0527	0.4855
A'	1148.3376	17.5932	1045.8524	37.0788	1045.5700	34.4862
A''	1197.3394	16.0981	1089.2259	19.1280	1086.4373	18.7812
A''	1398.6301	28.4526	1304.7481	1.6789	1293.2634	3.6883
A'	1506.4235	36.1852	1397.1531	4.8544	1394.8050	3.2979
A'	1527.2636	57.8844	1420.8653	100.0788	1408.5549	110.0893
A''	1572.9350	27.0063	1467.7627	21.6278	1460.6528	21.4803
A'	1595.9383	10.8243	1494.4958	10.1934	1486.2475	9.5627
A'	1881.5099	14.2069	1762.3327	58.1521	1751.8935	55.7420
A'	3178.5971	9.0171	3075.9689	28.3954	3042.7842	22.8274
A'	3256.7365	2.3120	3170.0991	9.3299	3128.3326	5.7316
A''	3297.8231	0.5398	3221.8085	7.1368	3176.9922	3.8884
A''	3403.7192	69.6134	3284.0981	116.4432	3254.2953	102.8518
A'	3442.8253	32.2933	3320.5787	54.2952	3290.9049	49.1324

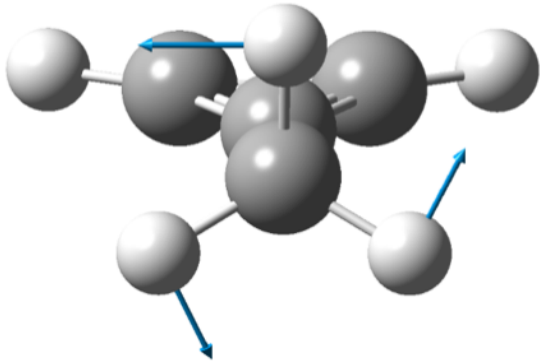

Figure S.1. The ν_{21} normal mode: the LAM corresponding to the torsion of the methyl group is represented by arrows.