

# Application of quasi-degenerate perturbation theory to the calculation of rotational energy levels of methane vibrational polyads

P. Cassam-Chenai,<sup>1, a)</sup> G. Rousseau,<sup>1</sup> A. Ilmane,<sup>1</sup> Y. Bouret,<sup>2</sup> and M. Rey<sup>3</sup>

<sup>1)</sup> *Univ. Nice Sophia Antipolis, CNRS, LJAD, UMR 7351, 06100 Nice, France.*

<sup>2)</sup> *Univ. Nice Sophia Antipolis, CNRS, LPMC, UMR 7336, 06100 Nice, France.*

<sup>3)</sup> *Groupe de Spectrométrie Moléculaire et Atmosphérique, CNRS UMR 6089, BP 1039, F-51687 Reims Cedex 2, France.*

(Dated: 17 April 2015)

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<sup>a)</sup>Electronic mail: [cassam@unice.fr](mailto:cassam@unice.fr)

## SUPPLEMENTARY MATERIAL

Table S1:

**MSP-VSCFCI/VSCFCI( $\nu_1 - \nu_3$ ,  $\nu_2 - \nu_4$ ; 32615, 16851)/VCI(0, 9343; 27535) and reference (F13P7) band centers (in  $\text{cm}^{-1}$ ). See main text for details.**

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VMFCI (27535  $\text{cm}^{-1}$ ) Ref. (F13P7) difference

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1310.744	1310.742	0.002
1533.315	1533.314	0.001
2587.285	2587.267	0.018
2614.249	2614.237	0.012
2624.740	2624.731	0.009
2830.626	2830.614	0.012
2846.078	2846.070	0.008
2916.478	2916.474	0.005
3019.477	3019.474	0.003
3063.818	3063.811	0.006
3065.172	3065.166	0.006
3871.051	3870.933	0.118
3909.300	3909.210	0.089
3920.729	3920.647	0.083
3931.293	3931.222	0.071
4102.106	4101.946	0.159
4129.284	4129.150	0.134
4133.735	4133.624	0.111
4143.183	4143.068	0.115

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VMFCI (27535 cm<sup>-1</sup>) Ref. (F13P7) difference

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4151.600	4151.498	0.103
4162.142	4162.044	0.099
4223.228	4223.215	0.013
4319.070	4319.057	0.013
4321.808	4321.790	0.019
4322.051	4322.034	0.018
4322.940	4322.921	0.019
4349.516	4349.407	0.109
4364.087	4363.994	0.093
4379.237	4379.154	0.084
4434.995	4434.982	0.014
4537.327	4537.314	0.012
4543.640	4543.624	0.016
4592.580	4592.507	0.073
4595.476	4595.411	0.065
4595.766	4595.701	0.065
5124.267	5123.631	0.636
5145.207	5144.629	0.578
5168.924	5168.468	0.456
5211.525	5211.157	0.368
5229.654	5229.343	0.310
5231.445	5231.127	0.319

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VMFCI (27535 cm<sup>-1</sup>) Ref. (F13P7) difference

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5241.392	5241.107	0.285
5373.367	5372.724	0.643
5391.502	5390.914	0.587
5425.773	5425.302	0.470
5431.427	5431.026	0.401
5438.476	5438.080	0.396
5445.591	5445.219	0.371
5463.729	5463.400	0.329
5493.085	5492.987	0.097
5521.194	5521.132	0.063
5533.191	5533.137	0.054
5588.550	5588.459	0.091
5606.766	5606.500	0.266
5614.273	5613.989	0.285
5614.735	5614.448	0.287
5615.289	5615.235	0.053
5615.387	5615.311	0.076
5619.345	5619.111	0.233
5625.702	5625.652	0.051
5627.256	5627.195	0.061
5644.091	5643.699	0.393
5655.640	5655.326	0.314

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VMFCI (27535 cm<sup>-1</sup>) Ref. (F13P7) difference

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5656.936	5656.589	0.347
5664.970	5664.677	0.294
5669.609	5669.295	0.313
5682.453	5682.183	0.270
5691.893	5691.625	0.267
5727.221	5727.153	0.068
5744.631	5744.586	0.046
5790.404	5790.365	0.039
5824.016	5823.959	0.057
5825.439	5825.400	0.039
5832.593	5832.514	0.079
5835.462	5835.394	0.068
5842.428	5842.388	0.039
5842.636	5842.593	0.042
5843.969	5843.919	0.050
5846.919	5846.873	0.046
5861.135	5861.059	0.077
5868.619	5868.402	0.217
5880.865	5880.607	0.258
5895.303	5895.069	0.234
5909.979	5909.755	0.224
5939.179	5939.163	0.016

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VMFCI (27535 cm<sup>-1</sup>) Ref. (F13P7) difference

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5952.297	5952.271	0.026
5968.288	5968.277	0.010
6004.460	6004.417	0.043
6043.857	6043.824	0.033
6054.503	6054.480	0.023
6060.449	6060.421	0.028
6065.742	6065.703	0.038
6118.020	6117.835	0.185
6119.619	6119.439	0.180
6124.665	6124.502	0.164

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RMS	0.385
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Table S2:

**P0-P6 quasi-degenerate space, order 2 perturbation theory and reference energy levels (in  $\text{cm}^{-1}$ ) of  $2\nu_3$  up to  $J = 7$  rotational quantum number. irrep.: “irreducible representation”. See main text for details.**

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J	irrep.	P0-P6	o2	Ref. (F13P7)	difference
1	F1	5978.86872	5978.86912	4.00e-04	
1	E	6014.42282	6014.42253	-2.90e-04	
1	F1	6014.43407	6014.43387	-2.00e-04	
1	F2	6015.13600	6015.13658	5.80e-04	
1	A2	6015.45383	6015.45497	1.14e-03	
1	F2	6054.02780	6054.02775	-5.00e-05	
1	F1	6054.16116	6054.16126	1.00e-04	
2	F2	6000.08210	6000.08327	1.17e-03	
2	E	6000.09006	6000.09121	1.15e-03	
2	F2	6034.77683	6034.77645	-3.80e-04	
2	F1	6034.79618	6034.79591	-2.70e-04	
2	A1	6034.82061	6034.82050	-1.10e-04	
2	F1	6035.88205	6035.88282	7.70e-04	
2	E	6035.89135	6035.89222	8.70e-04	
2	F2	6036.50223	6036.50425	2.02e-03	
2	A2	6074.26929	6074.26891	-3.80e-04	
2	F2	6074.45644	6074.45629	-1.50e-04	
2	E	6074.64707	6074.64714	7.00e-05	
2	F1	6074.84421	6074.84448	2.70e-04	

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J	irrep.	P0-P6	o2	Ref. (F13P7)	difference
2	A1	6075.03906	6075.03953	4.70e-04	
3	A2	6065.45609	6065.45564	-4.50e-04	
3	F2	6065.47680	6065.47642	-3.80e-04	
3	E	6065.49176	6065.49144	-3.20e-04	
3	F1	6065.53439	6065.53425	-1.40e-04	
3	A1	6066.97179	6066.97261	8.20e-04	
3	F1	6066.99260	6066.99366	1.06e-03	
3	F2	6067.00856	6067.00980	1.24e-03	
3	E	6067.89629	6067.89931	3.02e-03	
3	F1	6067.90049	6067.90353	3.04e-03	
3	F2	6104.88789	6104.88727	-6.20e-04	
3	F1	6105.23656	6105.23641	-1.50e-04	
3	E	6105.51398	6105.51409	1.10e-04	
3	F2	6105.78226	6105.78265	3.90e-04	
3	F1	6106.15283	6106.15359	7.60e-04	
4	F2	6106.48215	6106.48168	-4.70e-04	
4	F1	6106.51248	6106.51207	-4.10e-04	
4	E	6106.58121	6106.58093	-2.80e-04	
4	F2	6106.59529	6106.59506	-2.30e-04	
4	F1	6108.42637	6108.42743	1.06e-03	
4	E	6108.45772	6108.45919	1.47e-03	
4	F2	6108.46648	6108.46807	1.59e-03	



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J	irrep.	P0-P6	o2	Ref. (F13P7)	difference
4	A2	6108.47904	6108.48080	1.76e-03	
4	F2	6109.62744	6109.63147	4.03e-03	
4	F1	6109.63865	6109.64270	4.05e-03	
4	A1	6109.65244	6109.65653	4.09e-03	
4	E	6145.74446	6145.74344	-1.02e-03	
4	F1	6145.80070	6145.79975	-9.50e-04	
4	A1	6146.21253	6146.21223	-3.00e-04	
4	F1	6146.57171	6146.57172	1.00e-05	
4	F2	6146.83582	6146.83609	2.70e-04	
4	A2	6147.18397	6147.18454	5.70e-04	
4	F2	6147.62785	6147.62888	1.03e-03	
4	E	6147.68377	6147.68485	1.08e-03	
5	F1	6128.30444	6128.30923	4.79e-03	
5	E	6128.43992	6128.44450	4.58e-03	
5	F2	6128.85892	6128.86274	3.82e-03	
5	F1	6129.14876	6129.15218	3.42e-03	
5	E	6157.81763	6157.81697	-6.60e-04	
5	F1	6157.82839	6157.82773	-6.60e-04	
5	A1	6157.86355	6157.86295	-6.00e-04	
5	F1	6157.95804	6157.95743	-6.10e-04	
5	F2	6157.98626	6157.98567	-5.90e-04	
5	A2	6158.01034	6158.00977	-5.70e-04	

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J irrep.	P0-P6	o2	Ref. (F13P7)	difference
5	F2	6160.20811	6160.20932	1.21e-03
5	E	6160.21324	6160.21454	1.30e-03
5	F1	6160.25131	6160.25322	1.91e-03
5	F2	6160.26120	6160.26328	2.08e-03
5	A2	6161.67334	6161.67826	4.92e-03
5	F2	6161.68815	6161.69308	4.93e-03
5	E	6161.69865	6161.70358	4.93e-03
5	F1	6161.72993	6161.73489	4.96e-03
5	F2	6196.87977	6196.87808	-1.69e-03
5	F1	6196.98663	6196.98508	-1.55e-03
5	A1	6197.30356	6197.30227	-1.29e-03
5	F1	6197.96145	6197.96121	-2.40e-04
5	E	6198.23936	6198.23940	4.00e-05
5	F2	6198.52321	6198.52350	2.90e-04
5	A2	6199.21864	6199.21967	1.03e-03
5	F2	6199.51205	6199.51325	1.20e-03
5	F1	6199.61645	6199.61775	1.30e-03
6	A1	6192.98807	6192.99441	6.34e-03
6	F1	6193.31777	6193.32381	6.04e-03
6	F2	6193.67868	6193.68440	5.72e-03
6	A2	6194.29779	6194.30264	4.85e-03
6	F2	6194.87121	6194.87563	4.42e-03

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J	irrep.	P0-P6	o2	Ref. (F13P7)	difference
6	E	6194.97122	6194.97550	4.28e-03	
6	F2	6219.45496	6219.45378	-1.18e-03	
6	F1	6219.47706	6219.47589	-1.17e-03	
6	A1	6219.60195	6219.60055	-1.40e-03	
6	F1	6219.66472	6219.66339	-1.33e-03	
6	E	6219.69491	6219.69358	-1.33e-03	
6	F2	6219.73567	6219.73430	-1.37e-03	
6	A2	6222.29551	6222.29666	1.15e-03	
6	F2	6222.30142	6222.30273	1.31e-03	
6	F1	6222.30717	6222.30863	1.46e-03	
6	A1	6222.34505	6222.34725	2.20e-03	
6	F1	6222.34882	6222.35115	2.33e-03	
6	E	6222.35039	6222.35277	2.38e-03	
6	F2	6224.04062	6224.04620	5.58e-03	
6	F1	6224.06324	6224.06879	5.55e-03	
6	E	6224.12300	6224.12851	5.51e-03	
6	F2	6224.13369	6224.13920	5.51e-03	
6	A2	6258.26341	6258.26049	-2.92e-03	
6	F2	6258.34048	6258.33768	-2.80e-03	
6	E	6258.39352	6258.39082	-2.70e-03	
6	F1	6258.91890	6258.91669	-2.21e-03	
6	F2	6259.84444	6259.84382	-6.20e-04	

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J irrep.	P0-P6	o2	Ref. (F13P7)	difference
6	E	6260.13940	6260.13903	-3.70e-04
6	F1	6260.41911	6260.41903	-8.00e-05
6	F2	6261.38435	6261.38535	1.00e-03
6	E	6261.86122	6261.86242	1.20e-03
6	F1	6261.91178	6261.91304	1.26e-03
6	A1	6261.98465	6261.98597	1.32e-03
7	F1	6269.42277	6269.43037	7.60e-03
7	E	6269.95729	6269.96471	7.42e-03
7	F2	6270.37772	6270.38514	7.42e-03
7	A2	6271.79778	6271.80479	7.01e-03
7	F2	6272.21209	6272.21816	6.07e-03
7	F1	6272.41698	6272.42263	5.65e-03
7	A2	6291.36944	6291.36725	-2.19e-03
7	F2	6291.38885	6291.38667	-2.18e-03
7	E	6291.40080	6291.39865	-2.15e-03
7	F1	6291.59991	6291.59720	-2.71e-03
7	F2	6291.70511	6291.70253	-2.58e-03
7	E	6291.76985	6291.76710	-2.75e-03
7	F1	6291.79295	6291.79019	-2.76e-03
7	F2	6294.67864	6294.67972	1.08e-03
7	E	6294.68453	6294.68584	1.31e-03
7	F1	6294.68544	6294.68688	1.44e-03

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J irrep.	P0-P6	o2	Ref. (F13P7)	difference
7	A1	6294.68670	6294.68833	1.63e-03
7	F2	6294.72068	6294.72317	2.49e-03
7	F1	6294.72121	6294.72363	2.42e-03
7	E	6296.69332	6296.69913	5.81e-03
7	F1	6296.70175	6296.70753	5.78e-03
7	A1	6296.72655	6296.73226	5.71e-03
7	F1	6296.82124	6296.82683	5.59e-03
7	F2	6296.84500	6296.85054	5.54e-03
7	A2	6296.86613	6296.87164	5.51e-03
7	F2	6330.01416	6330.00945	-4.71e-03
7	F1	6330.08421	6330.07961	-4.60e-03
7	E	6330.79575	6330.79197	-3.78e-03
7	F2	6330.89423	6330.89058	-3.65e-03
7	A2	6331.94810	6331.94650	-1.60e-03
7	F2	6332.24950	6332.24818	-1.32e-03
7	F1	6332.51103	6332.50998	-1.05e-03
7	A1	6332.79522	6332.79444	-7.80e-04
7	F1	6333.88574	6333.88629	5.50e-04
7	E	6333.97400	6333.97464	6.40e-04
7	F2	6334.59698	6334.59783	8.50e-04
7	F1	6334.66138	6334.66231	9.30e-04

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J irrep. P0-P6 o2 Ref. (F13P7) difference

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RMS 0.003

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