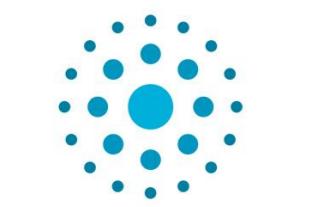
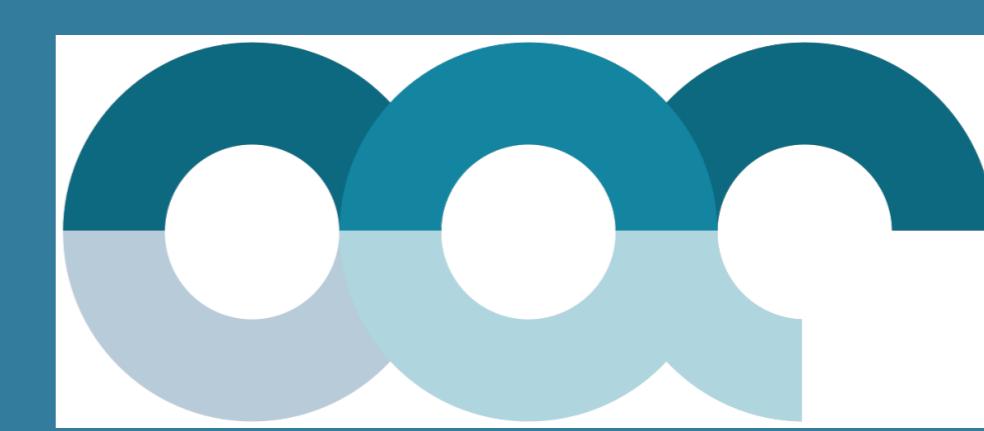


Theoretical study of naphtalene neutral and cation vibrational spectra with the VMFCI method



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Polycyclic aromatics hydrocarbons (PAHs) are thought to be abundant throughout the universe as the ubiquitous so called "aromatic infrared bands" (AIBs) are attributed to PAHs, ionised or neutral, and their derivatives. We studied the smallest PAH, the naphtalene, which is often taken as a model for larger ones.

We investigated different criteria to build an efficient vibrational contraction-truncation scheme, which we present here. Our ultimate goal is to compute, by using the Vibrational Mean Field Contraction Iteration (VMFCI) method [1] implemented in the code CONVIV [2], the infrared spectra of the neutral and cation forms of the naphtalene.

I. General context

A. Why study naphtalene ?

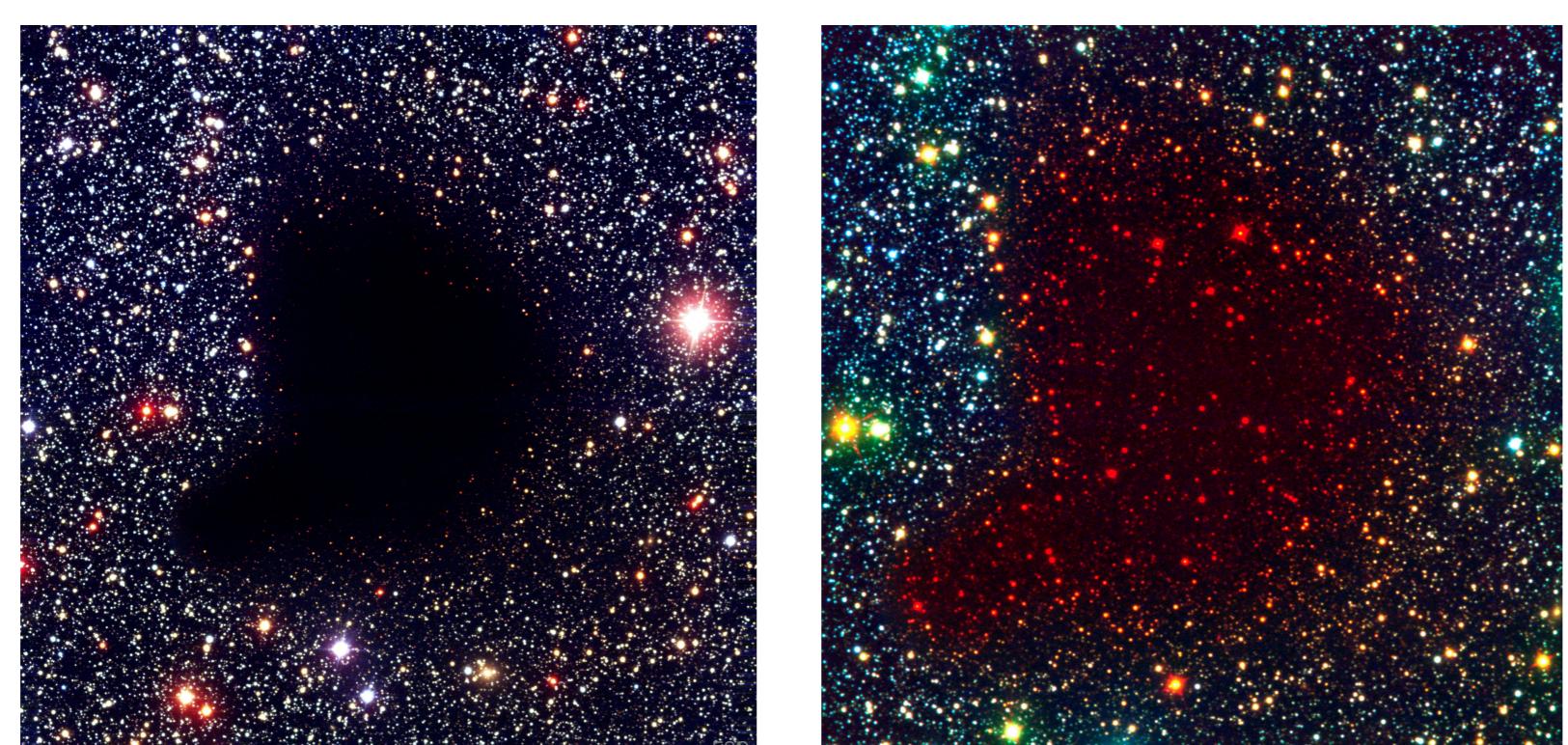


Figure 1: Visible (left) and Infrared (right) dark molecular cloud Barnard 68

- Model for bigger PAHs
- Cyanonaphthalene discovered in the dark molecular cloud TMC-1
- The most precise and recent study by Chakraborty et. al. [3] has established that :
 - An anharmonic calculation is necessary ($RMS \approx 100cm^{-1}$)
 - VSCF is still too far from experiment ($RMS \approx 26 - 37cm^{-1}$)
 - VPT2 is able to reproduce the CH band features
- VCCM is better however still have weaknesses :
 - only 8 basis function/modes
 - only 4 excitation quanta
 - 13 modes with low frequencies ($< 750cm^{-1}$) neglected
 - ν_{46} far from experimental frequency
- Anharmonic calculations VMFCI to revisit Naphtalene and its cation

B. How a molecule vibrates ?

- 3 types of nuclear motion : translational, rotational and vibrational
- Translations decoupled
- Rotation neglected
- A semi-rigid molecule is characterised by its equilibrium geometry.
- A non-linear molecule has $3N_{atom} - 6$ modes of vibrations

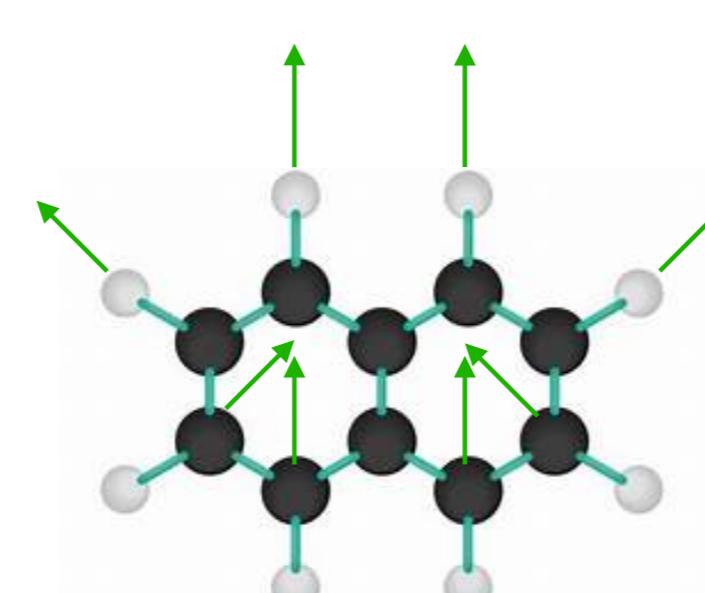


Figure 2: An example of naphtalene's vibration : the ν_{17} CH stretching mode

C. The effective Hamiltonian

- $\hat{H}_{active}^{eff} = \hat{H}_{vib\ active} + \langle \bigotimes_{I_\gamma \in spectators} \varphi_{I_\gamma}^0 | \hat{H}_{vib} - \hat{H}_{vib\ active} | \bigotimes_{I_\gamma \in spectators} \varphi_{I_\gamma}^0 \rangle$.

II. The vibrational contraction scheme

```
out_napht 0:4524:Step 12 ZPE (1-2) > 32000.58599768
out_napht 15:3600:Step 12 ZPE (1-17) > 32002.27371854
out_napht 32:3600:Step 12 ZPE (1-34) > 32003.60125469
out_napht_13:5121:Step 12 ZPE (1-15) > 32005.36187509
out_napht_16:8823:Step 12 ZPE (2-34) > 32005.73273673
```

Figure 3: First criterion for choosing the contractions : An extract of the ZPE file for the pair test of the twelfth step

14	1	15	38	787,142860	776,857258	10,28560200000004	0,8787892936540906
10	1	11	38	888,413633	880,291528	8,122105000000033	0,6132212270198147
39	1	46	38	841,105109	833,210575	7,8945340000000215	0,629667104913857
9	1	10	38	1019,929209	1015,126739	4,8024699999971	0,31489720405720545
4	7	5	8	1376,985592	1372,274329	4,71126299999917	0,22861695253411596

Figure 4: Second Criterion for choosing the contractions : An extract of the file which contained the differences between frequencies for the pair test of the fourteenth step

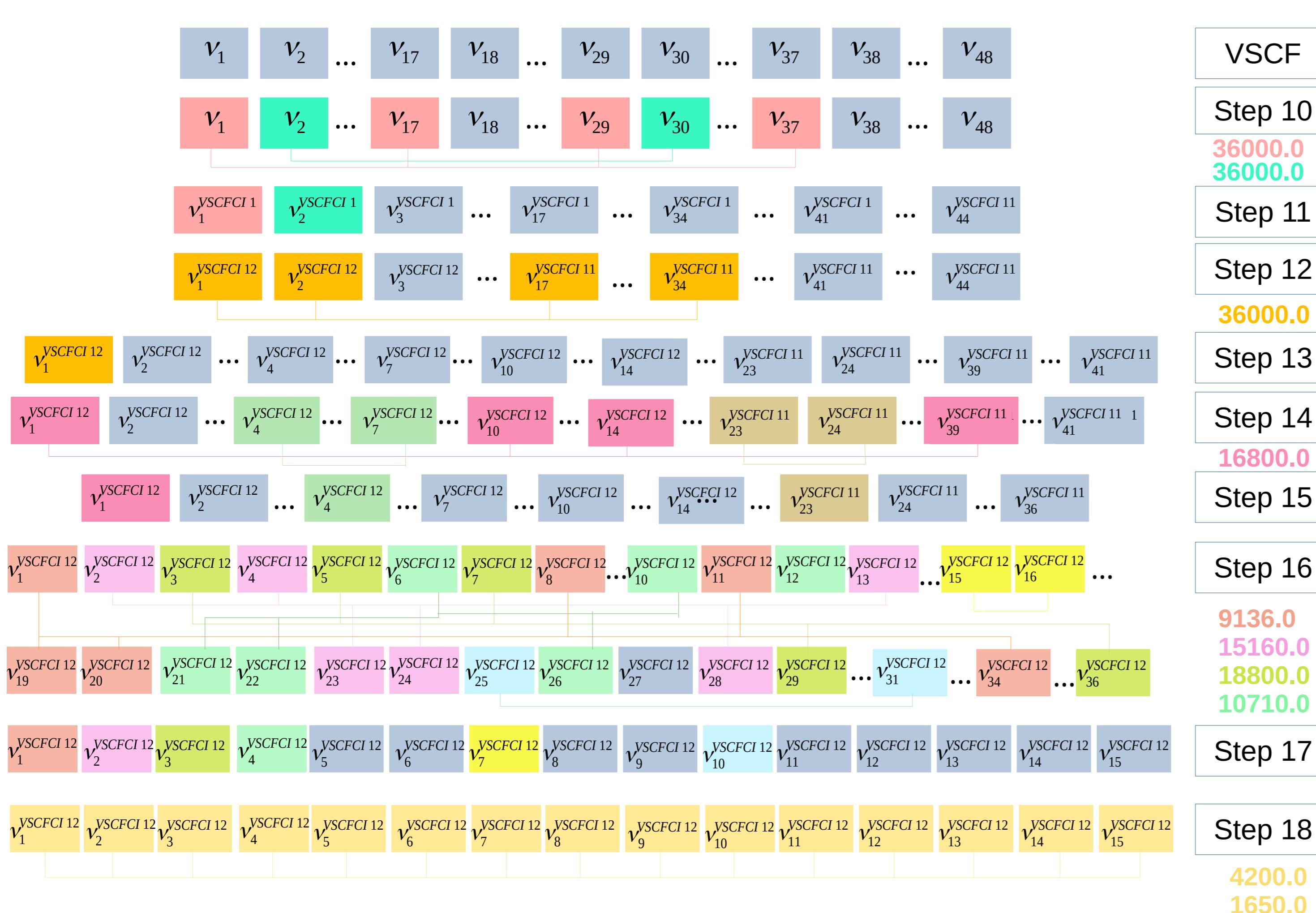


Figure 5: The vibrational contraction-truncation schemes for the neutral form of the naphtalene

III. Vibrational spectra

Table 1: Frequencies obtained for naphtalene's neutral form and the ZPE associated to every SCF converged step, all in cm^{-1}

Irreducible Modes representation	ν_{VSCF}	$\nu_{VSCFCI11}$	$\nu_{VSCFCI13}$	$\nu_{VSCFCI15}$	$\nu_{VSCFCI17}$	
b_{1u}	ν_{17}	3088.6	3034.1	2969.9	2975.9	2986.2
	ν_{18}	3070.9	3071.5	2952.3	2951.6	2966.8
	ν_{19}	1612.7	1612.6	1612.4	1612.3	1607.8
	ν_{20}	1400.3	1399.9	1399.4	1399.3	1399.0
	ν_{21}	1270.2	1270	1269.6	1269.5	1269.4
	ν_{22}	1141.4	1141.2	1140.9	1140.8	1140.6
	ν_{23}	799.2	799.1	799	799.0	798.9
	ν_{24}	366.2	366.1	366	365.9	365.9
b_{2u}	ν_{29}	3100.5	3034.2	2983.6	2990.4	2997.9
	ν_{30}	3073.2	3044.0	2956.3	2955.0	2970.8
	ν_{31}	1523.8	1523.7	1523.4	1523.3	1520.7
	ν_{32}	1375.2	1375	1374.7	1374.6	1370.6
	ν_{33}	1220.7	1220.4	1220.2	1220.1	1218.3
	ν_{34}	1161.3	1161.1	1160.6	1160.5	1160.3
	ν_{35}	1024	1023.9	1023.7	1023.7	1021.9
	ν_{36}	626.1	626	626	626.0	625.9
b_{3u}	ν_{45}	1006.5	1006.1	1005.2	1005.4	963.0
	ν_{46}	842.4	841.8	841.1	818.1	788.9
	ν_{47}	503.4	503.2	502.7	502.9	510.4
	ν_{48}	190.6	190.4	190.3	190.5	189.8

ZPE 32029.8 32007.3 31958.4 31943.0 31878.2

Table 2: Frequencies obtained for naphtalene's cation form and the ZPE associated to every SCF converged step, all in cm^{-1}

Irreducible Modes representation	ν_{VSCF}	$\nu_{VSCFCI11}$	$\nu_{VSCFCI13}$	$\nu_{VSCFCI15}$	
b_{1u}	ν_{17}	3109.1	3033.2	2997.6	3004.1
	ν_{18}	3093.7	3094.6	2982.3	2987.2
	ν_{19}	1528.8	1528.5	1528.3	1527.7
	ν_{20}	1414.1	1413.6	1413.3	1413.0
	ν_{21}	1286.5	1286.3	1286.0	1285.8
	ν_{22}	1115.0	1114.7	1114.5	1114.4
	ν_{23}	798.7	798.6	798.6	798.4
	ν_{24}	360.2	360.1	360.0	359.9
b_{2u}	ν_{29}	3120.0	3036.1	3009.2	3015.3
	ν_{30}	3095.1	3055.1	2984.1	2983.1
	ν_{31}	1542.7	1542.4	1542.2	1542.0
	ν_{32}	1396.1	1395.9	1395.8	1393.9
	ν_{33}	1223.1	1222.9	1222.6	1222.1
	ν_{34}	1185.5	1185.0	1184.8	1184.4
	ν_{35}	1025.9	1025.8	1025.7	1025.6
	ν_{36}	600.1	600.1	600.1	600.0
b_{3u}	ν_{45}	1026.8	1026.1	1025.5	1025.5
	ν_{46}	825.3	824.3	823.8	789.2
	ν_{47}	441.7	441.5	441.1	439.9
	ν_{48}	173.3	173.1	173.0	172.9

ZPE 31935.8 31902.0 31867.8 31842.6

Conclusion and perspectives

We have investigated vibrational contraction schemes for neutral and cationic forms of naphtalene. We have first used the ZPE lowering criteria, as VMFCI is a variational method, the lower ZPE, the better the calculation. Then, we also used a frequency variation criterion (up to fifth excited state frequencies). Our work is still in progress for the last step, the VCI one, and we are currently trying to determine the product basis set truncation scheme which gives the best convergence. In parallel, we will use an electric dipole moment hypersurface to calculate the intensities and plot theoretical infrared spectra.

References

- [1] P. Cassam-Chenai, J. Lièvin, J. Comp. Chem. 27 (2006) 627-640.
- [2] <https://forge.oca.eu/trac/conviv>
- [3] S Chakraborty, S. Banik, P. K. Das, J. Phys. Chem A120 (2016) 9707-9718.



VSCF : vibrational self consistent field; RMS : root mean square; VPT2 : vibrational second order perturbation theory VCCM : vibrational coupled cluster method ZPE : zero point of energy; VCI : vibrational configuration interaction