The Vibrational Mean-Field Configuration Interaction method: theory and applications

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Resolution of the Schrödinger equation of interacting quantum objects

electrons

nucleons

Collective nuclear motions (rotation/vibration)

undistinguishable

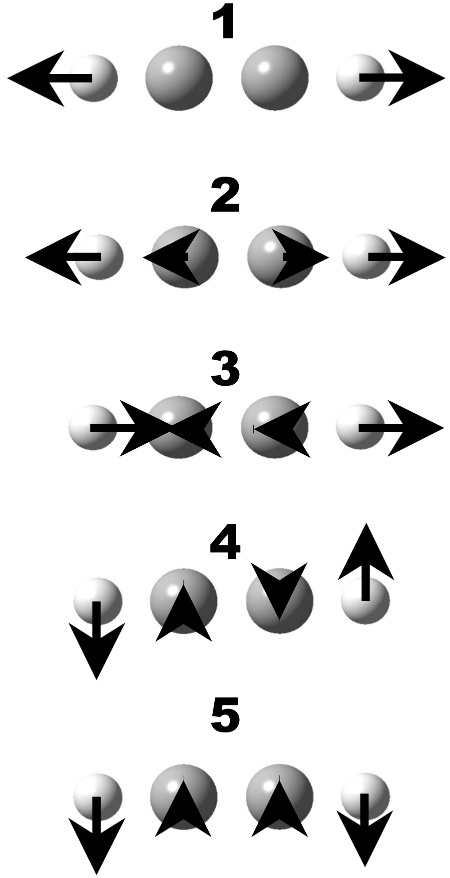
permutational symmetry

distinguishable

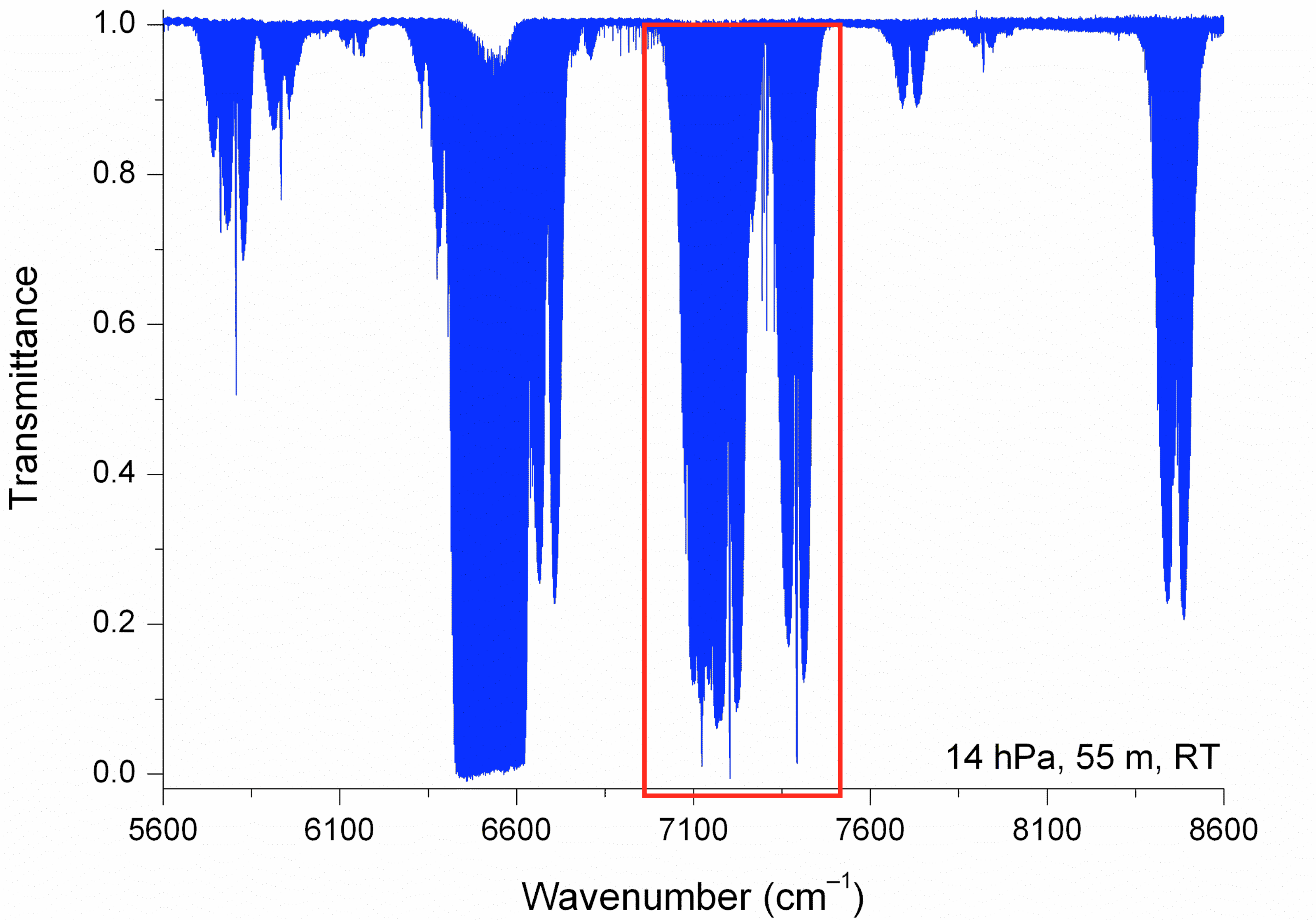
common methodological strategy → perturbation

variation (SCF / CI)

H − C ≡ C − H

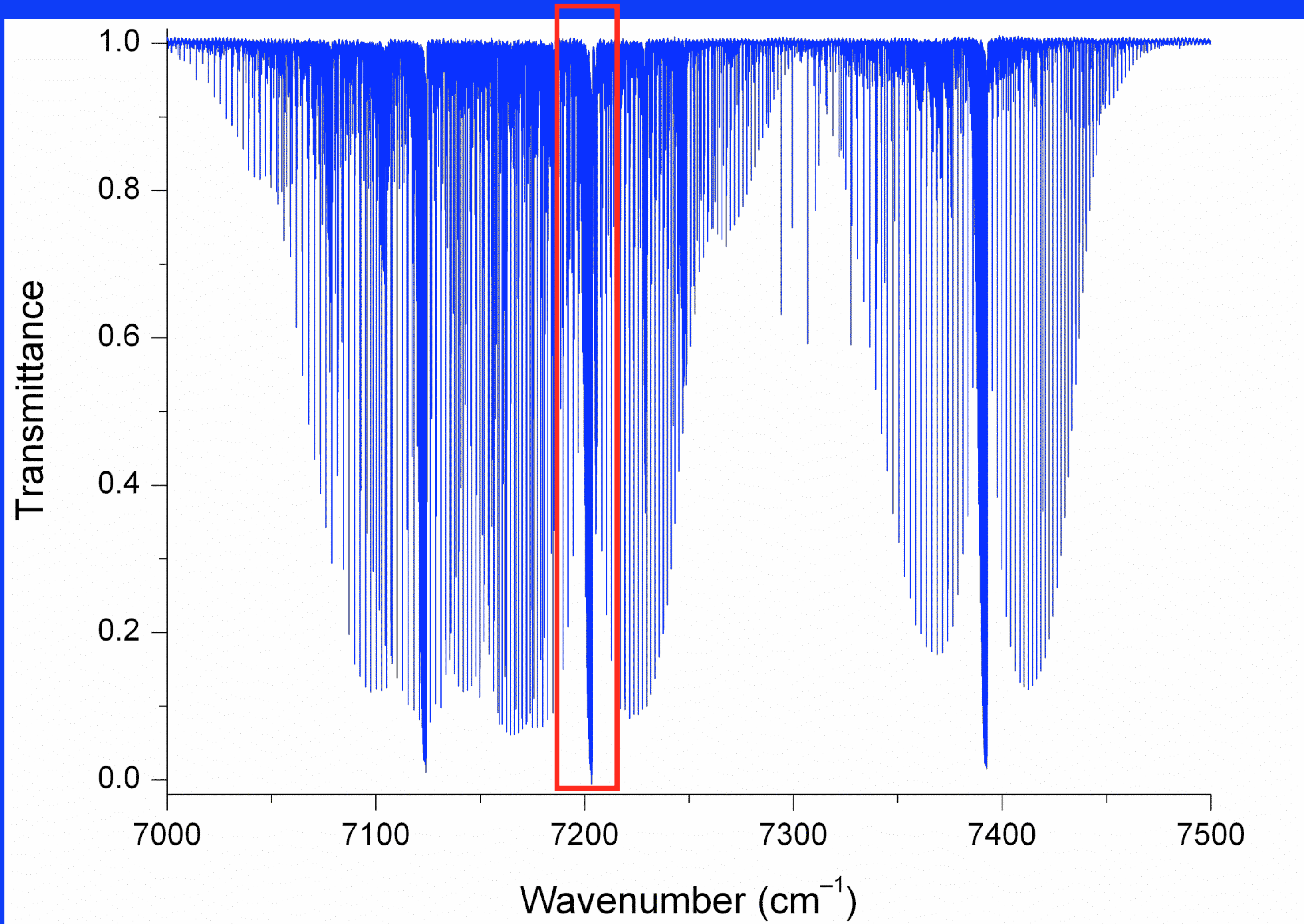


Mode	Symmetry	$^{12}C_2H_2$	$^{12}C_2D_2$	$^{13}C_2H_2$	$^{12}C_2HD$	$^{12}C^{13}CH_2$	
1	$\sigma^{+}_{(g)}$	3397.12	2717.22	3374.90	3387.33	3389.12	cm^{-1}
2	$\sigma^{+}_{(g)}$	1981.80	1768.07	1918.04	1859.36	1950.11	cm^{-1}
3	$\sigma^{+}_{(u)}$	3316.86	2455.11	3305.55	2605.83	3310.02	cm^{-1}
4	$\pi_{(g)}$	608.73	509.24	599.92	517.40	604.47	cm^{-1}
5	$\pi_{(u)}$	729.08	538.00	727.23	676.09	728.27	cm^{-1}



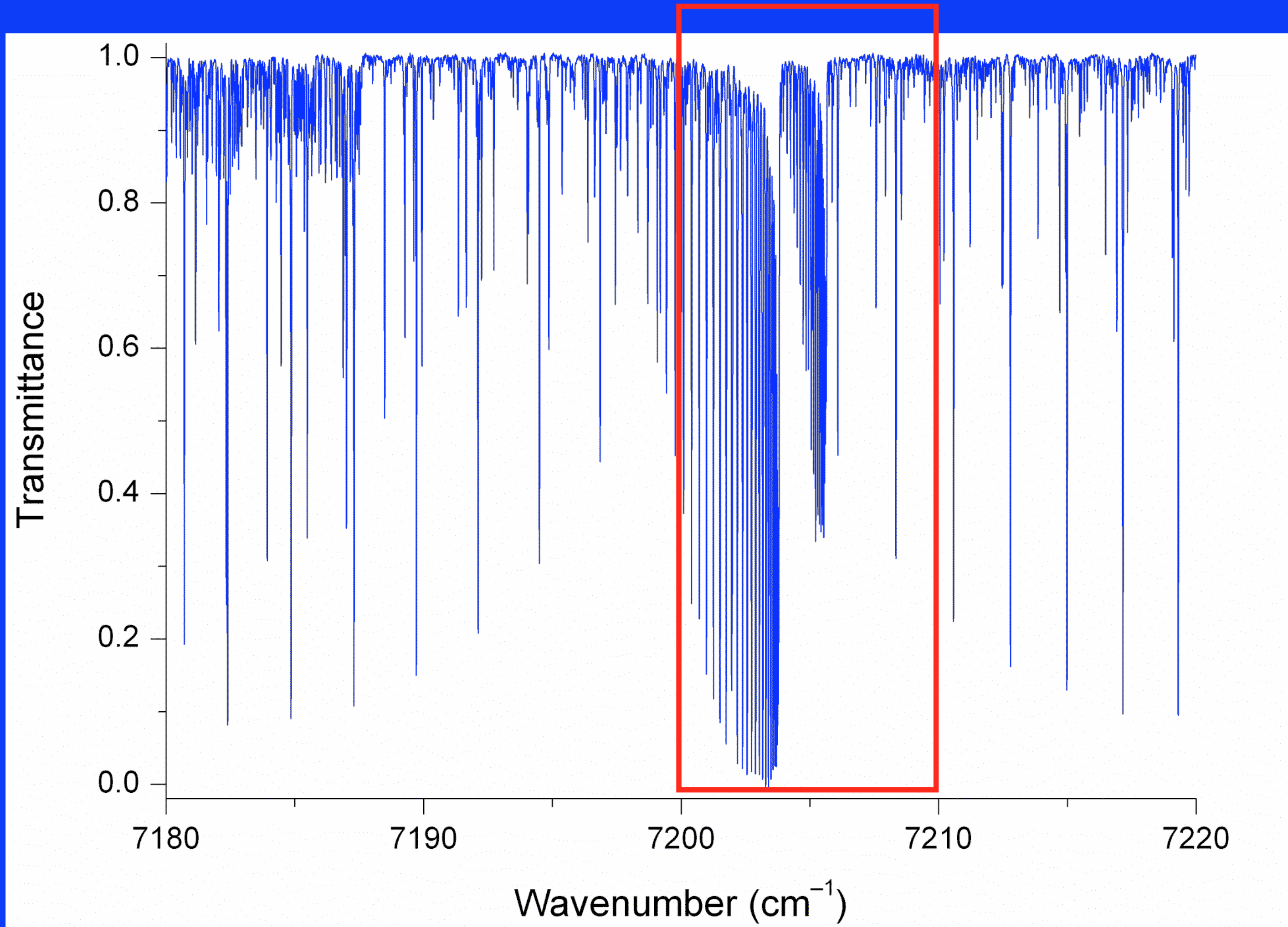
1.0
0.8
0.6
0.4
0.2
0.0
Transmittance
14 hPa, 55 m, RT
5600
6100
6600
7100
7600
8100
8600
Wavenumber (cm^{-1})

$^{12}C^{13}CH_2$



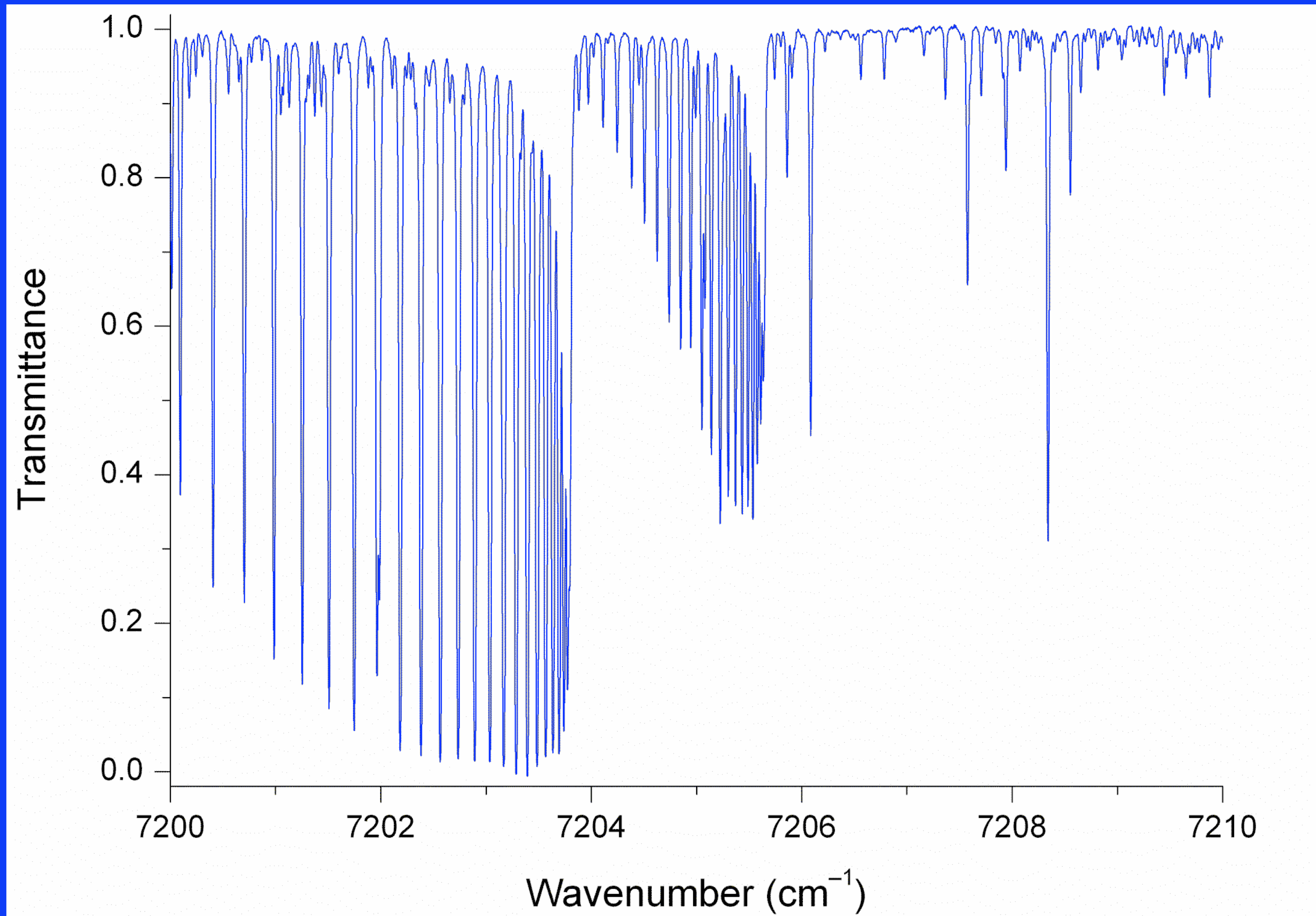
Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
7000
7100
7200
7300
7400
7500
Wavenumber (cm^{-1})

$^{12}C^{13}CH_2$



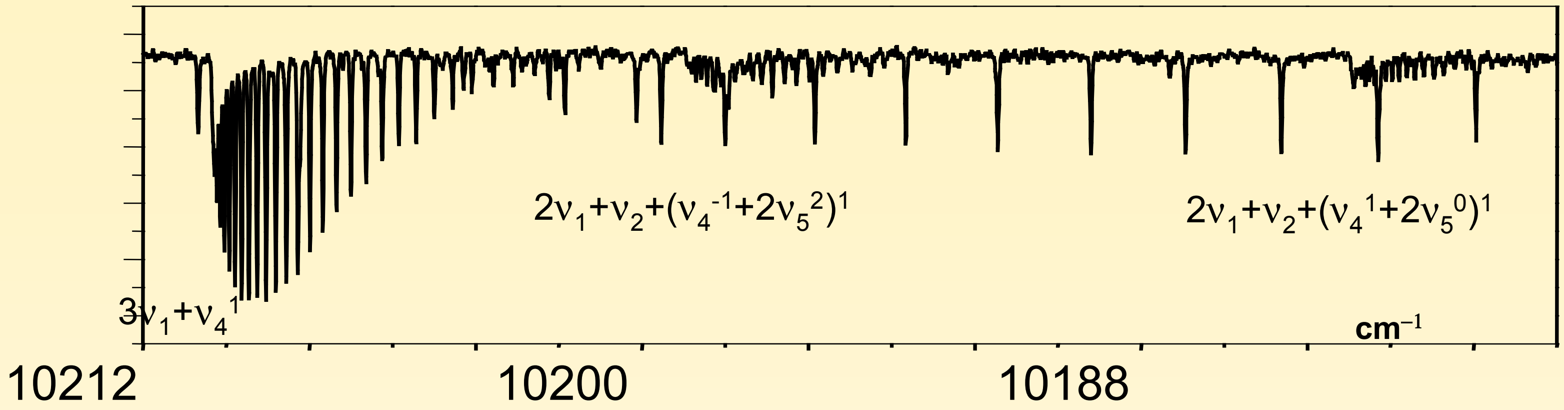
Transmittance
1.0
0.8
0.6
0.4
0.2
0.0
7180
7190
7200
7210
7220
Wavenumber (cm−1)

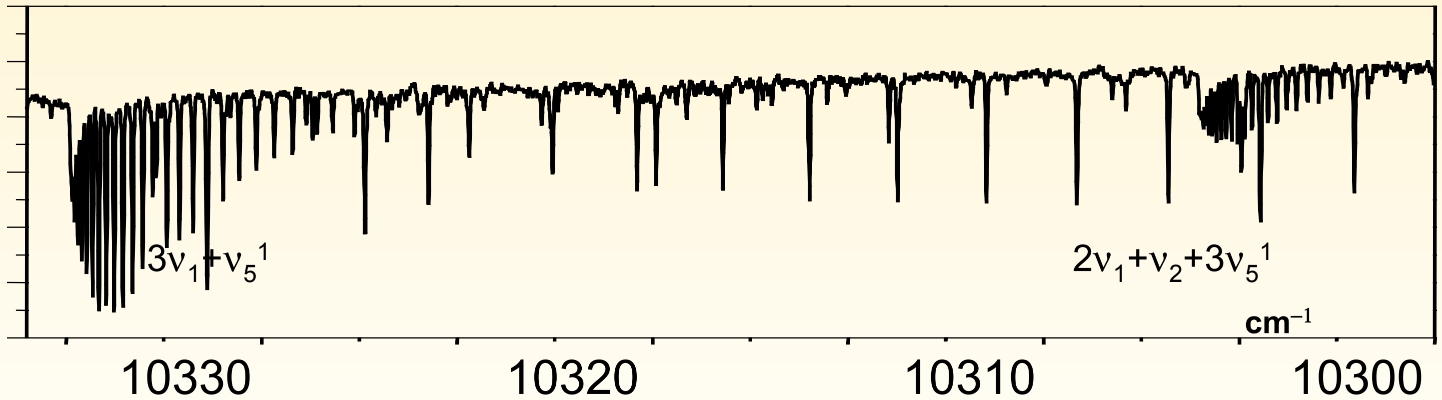
$^{12}C^{13}CH_2$


1.0
0.8
0.6
0.4
0.2
0.0
Transmittance
7200
7202
7204
7206
7208
7210
Wavenumber (cm^{-1})

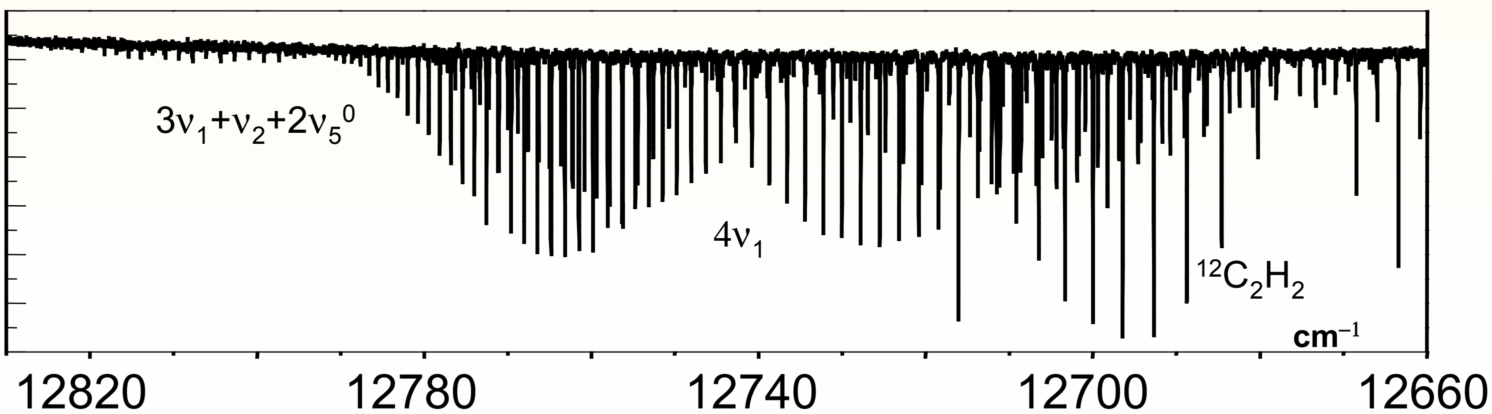
$^{12}C^{13}CH_2$

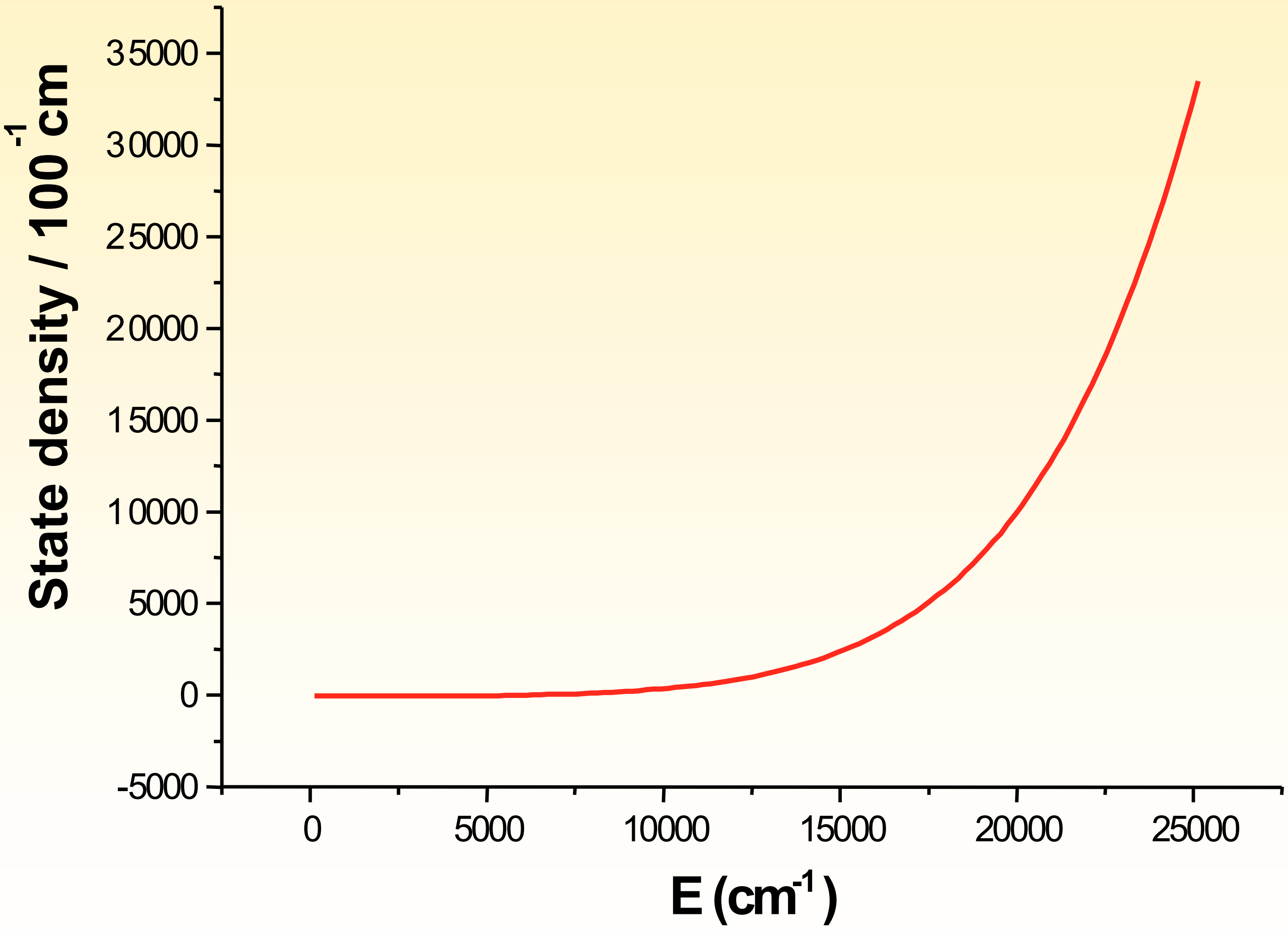
C_2HD





« The acetylene ground state saga »
M. Herman
Mol. Phys.
in press





State density / 100 cm-1
35000
30000
25000
20000
15000
10000
5000
0
-5000
0
5000
10000
15000
20000
25000
E (cm-1)

- Global fits are performed on isotopologues of acetylene (> 15000 lines for $C^{13}CH_2$)

Fayt *et al*, JCP **126** (2007) 114303

- HITRAN data base collects lines in atmospherical absorption windows

HIgh-resolution **TRAN**smission molecular absorption

HITRAN-2004: > 1.7 millions of spectral lines for 37 molecules

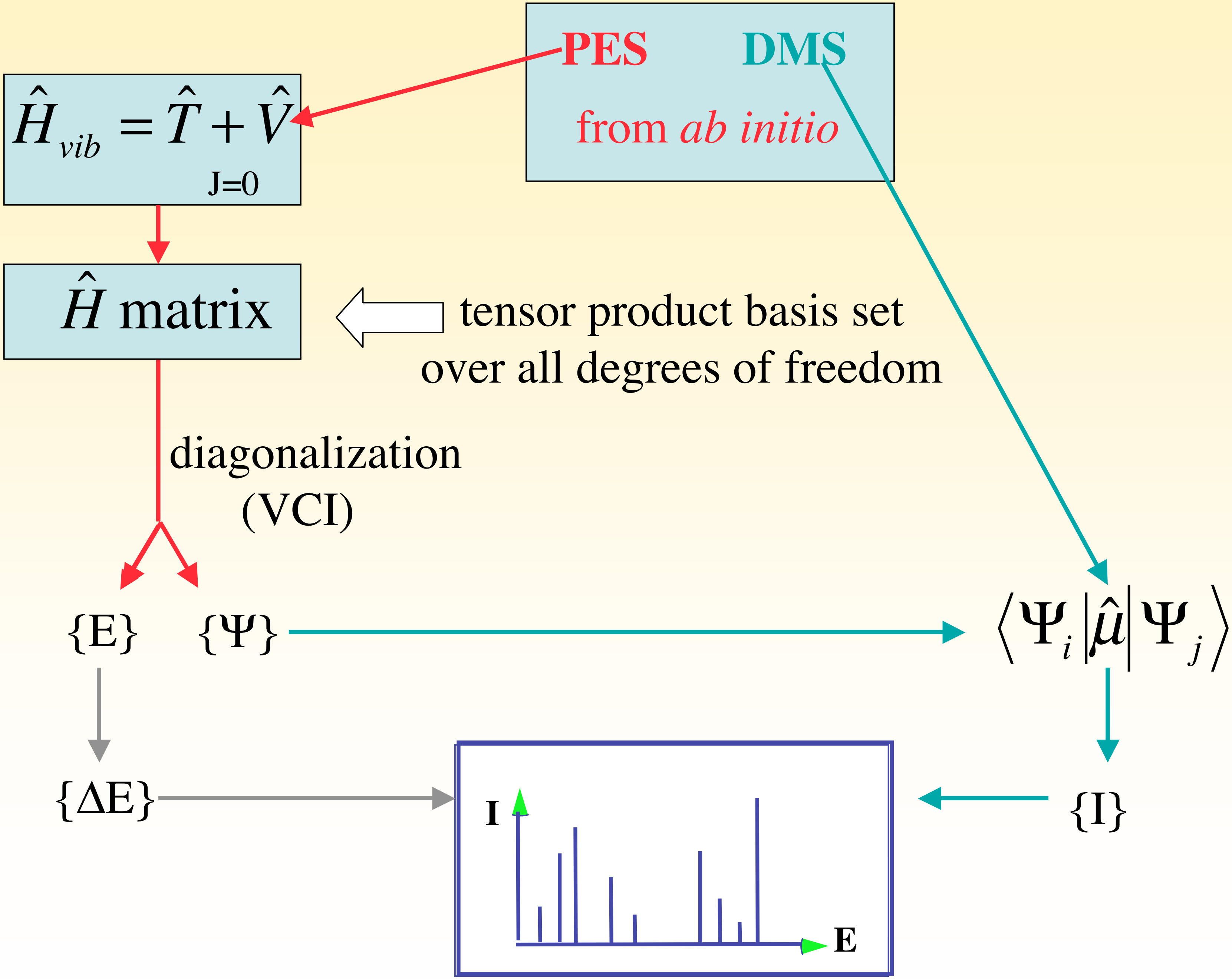
BUT

- spectroscopic information is still sparse for many other molecules

- fitted spectroscopic parameters may be biased and extrapolations can be hazardous

a real challenge for theory

Variational resolution of the vibration problem



Variational treatment of N interacting objets

1object b.s.

Mean field
SCF

1 object b.s. with
effective coupling

symmetrized tensor
product N objects b.s.

« configurations »

SCF / CI

truncation

diagonalization
of the CI matrix

Goal: obtain optimized b.s.
$\rightarrow$ better convergence of CI

vibrational VSCF

Bowman, Gerber, Carney (1978)

single-configuration $\left|\Psi\right\rangle = \phi_{v_1}(Q_1)\phi_{v_2}(Q_2)\ldots\phi_{v_{3N-6}}(Q_{3N-6})$

product of modals

mean field

$$[\, h_j(Q_j) + \overbrace{\left\langle \prod_{i\neq j}\phi_{v_i}(Q_i) \middle| (H-h_j) \middle| \prod_{i\neq j}\phi_{v_i}(Q_i) \right\rangle}^{\text{mean field}} - \varepsilon_{v_j} \,]\, \phi_{v_j}(Q_j) = 0$$

(for j = 1 to 3N-6)

$$H = \sum_i h_i + \sum_{i,j} h_{ij} + \sum_{i,j,k} h_{ijk} + \ldots$$

!! 1 variational space / mode

Electrons

MCSCF / MRCI
CASSCF / MRCI

= standards of Quantum Chemistry

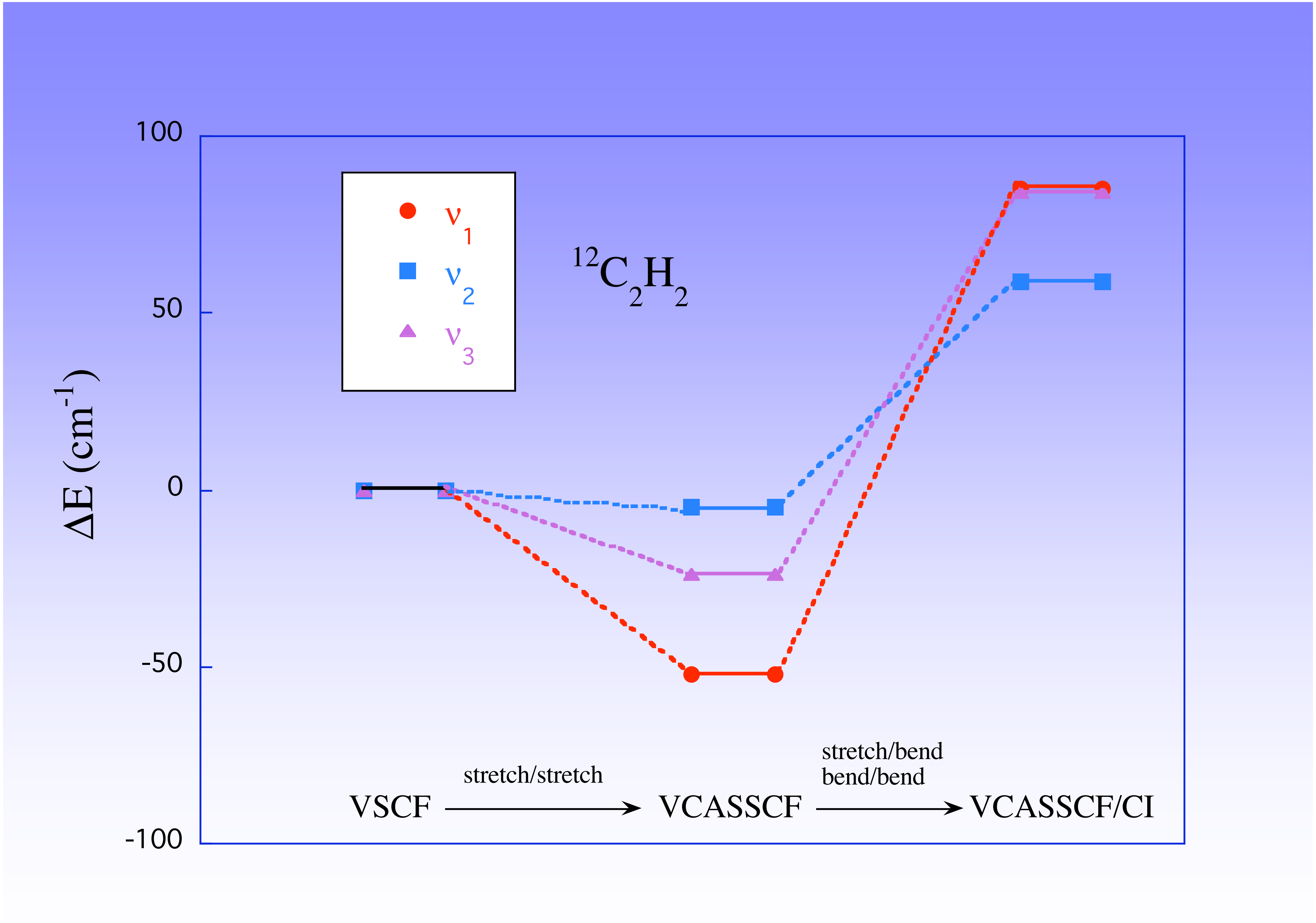
Vibrations

VMCSCF F. Culot and J. Liévin, Theoret. Chim. Acta **89**, 227 (1994)

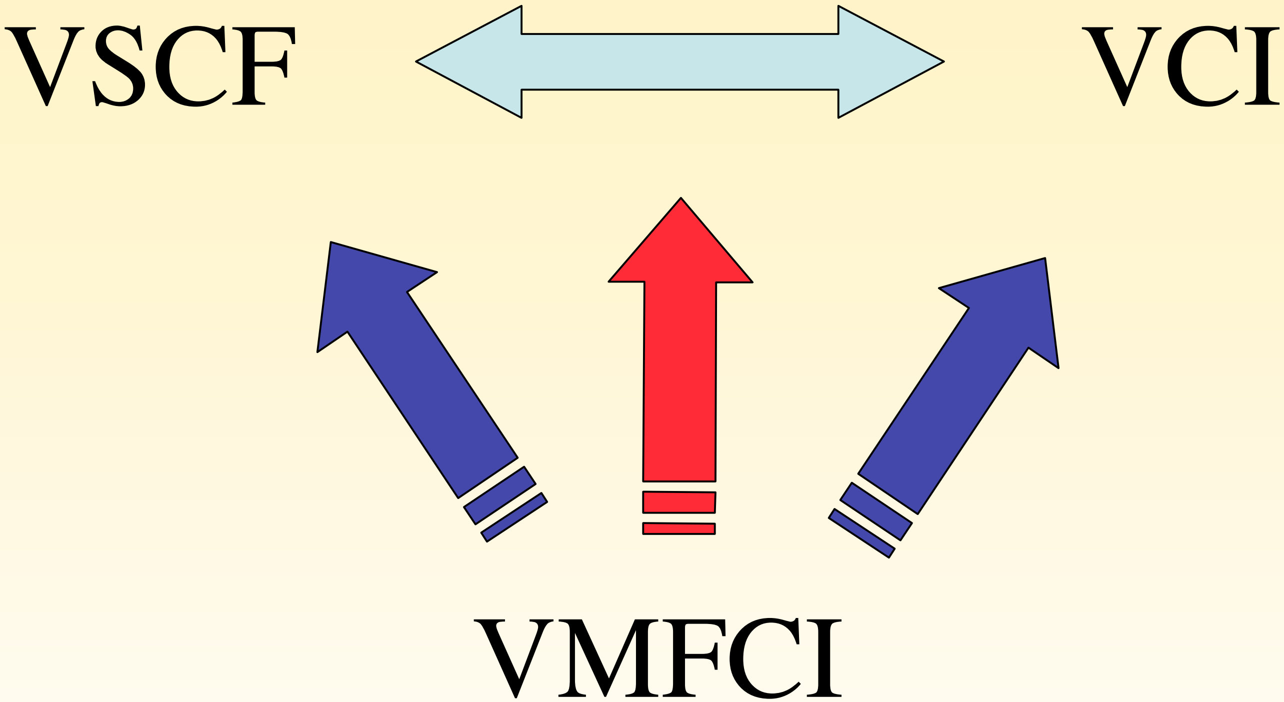
VCASSCF F. Culot, F. Laruelle and J. Liévin, Theoret. Chim. Acta **92**, 211 (1995)

→ super-CI algorithm based on the **generalized Brillouin theorem**

Analysis of vibrational resonances
Analysis of stretch-bends couplings in water and acetylene



100
50
0
-50
-100
ΔE (cm^{-1})
ν_1
ν_2
ν_3
$^{12}C_2H_2$
stretch/stretch
stretch/bend
bend/bend
VSCF
VCASSCF
VCASSCF/CI



Vibrational Mean Field Configuration Interaction

Hierarchical coupling
Mean field optimization
Energy truncation

⇒ compact VCI functions

P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245 (2003)
P. Cassam-Chenaï and J. Liévin, J. Comput. Chem. **27**, 608 (2006)

The VMFCI method

$J = 0$ Hamiltonian of an n-oscillator system :

$$H = \sum_{i_1} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1, i_2} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \ldots + h_n(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}, \cdots, Q_{i_n}, P_{i_n})$$

Contraction of the n modes into q sets $I_1, I_2, \ldots, I_q$ of $p_1, p_2, \ldots, p_q$ modes:

$$(I_1, I_2, \ldots, I_q) \begin{cases} \{i_1^1, i_2^1, \ldots, i_{p_1}^1\} \\ \{i_1^2, i_2^2, \ldots, i_{p_2}^2\} \\ \cdots \\ \{i_1^q, i_2^q, \cdots, i_{p_q}^q\} \end{cases} \quad \text{with} \quad \sum_{i=1}^{q} p_i = n$$

Each contraction is described by a product basis set:

$$\{\phi_{V_1}, \phi_{V_2}, \ldots \phi_{V_q}\} \quad \text{with} \quad \phi_{V_j} = \prod_{x=1}^{p_j} \phi_{v_x^j}(Q_{i_x^j})$$

Mean-field treatment for contraction I_j:

Partial Hamiltonian for contraction I_j:

$$H_j = \sum_{i_1 \in I_j} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1, i_2 \subset I_j} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \ldots$$

Mean-field Hamiltonian for I_j:

$$H_j^{VSCF} = H_j + < \prod_{I_k \neq I_j} \phi_0(Q_{i_1}, \ldots, Q_{i_{p_k}}) \left| H - H_j \right| \prod_{I_k \neq I_j} \phi_0(Q_{i_1}, \ldots, Q_{i_{p_k}}) >$$

Reference state for the mean-field

This Hamiltonian is diagonalized on the full product basis set of I_j

***n*-modes mean-field calculation:** successive application of the mean-field treatment to each contraction $I_1, I_2, \ldots, I_q$

***VSCF* calculation:** iterate the *n*-modes mean-field treatment until convergence

***VMFCI* calculation:**
apply the above mean-field (or SCF) approach to a set of succesive *n*-modes contractions.

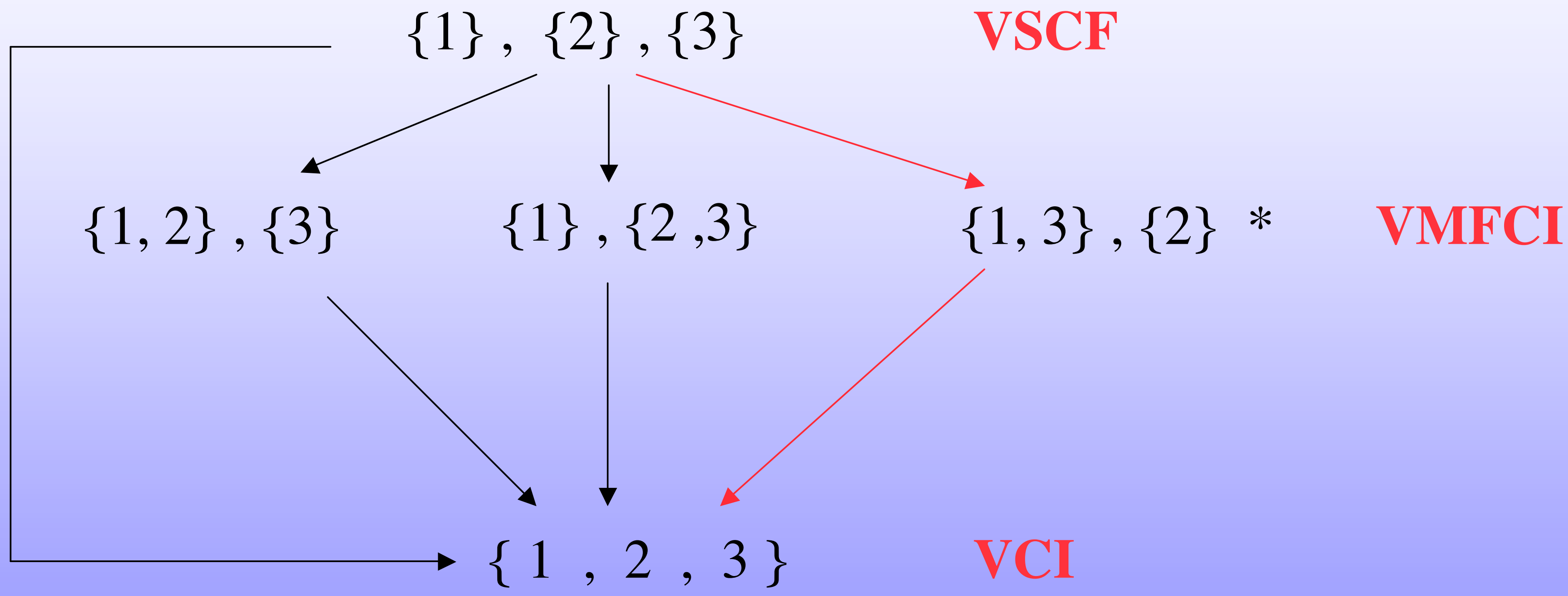
The last contraction step correspond to the full-CI.

The VMFCI method is implemented in the fortran 95 CONVIV program

- Watson Hamiltonian in normal coordinates
- Polynomial form of the potential and Morse terms
- Harmonic oscillator basis sets

Example for water

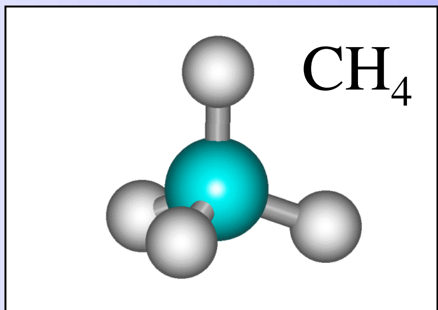
{1} sym. stretch | {2} bend | {3} anti-sym. stretch



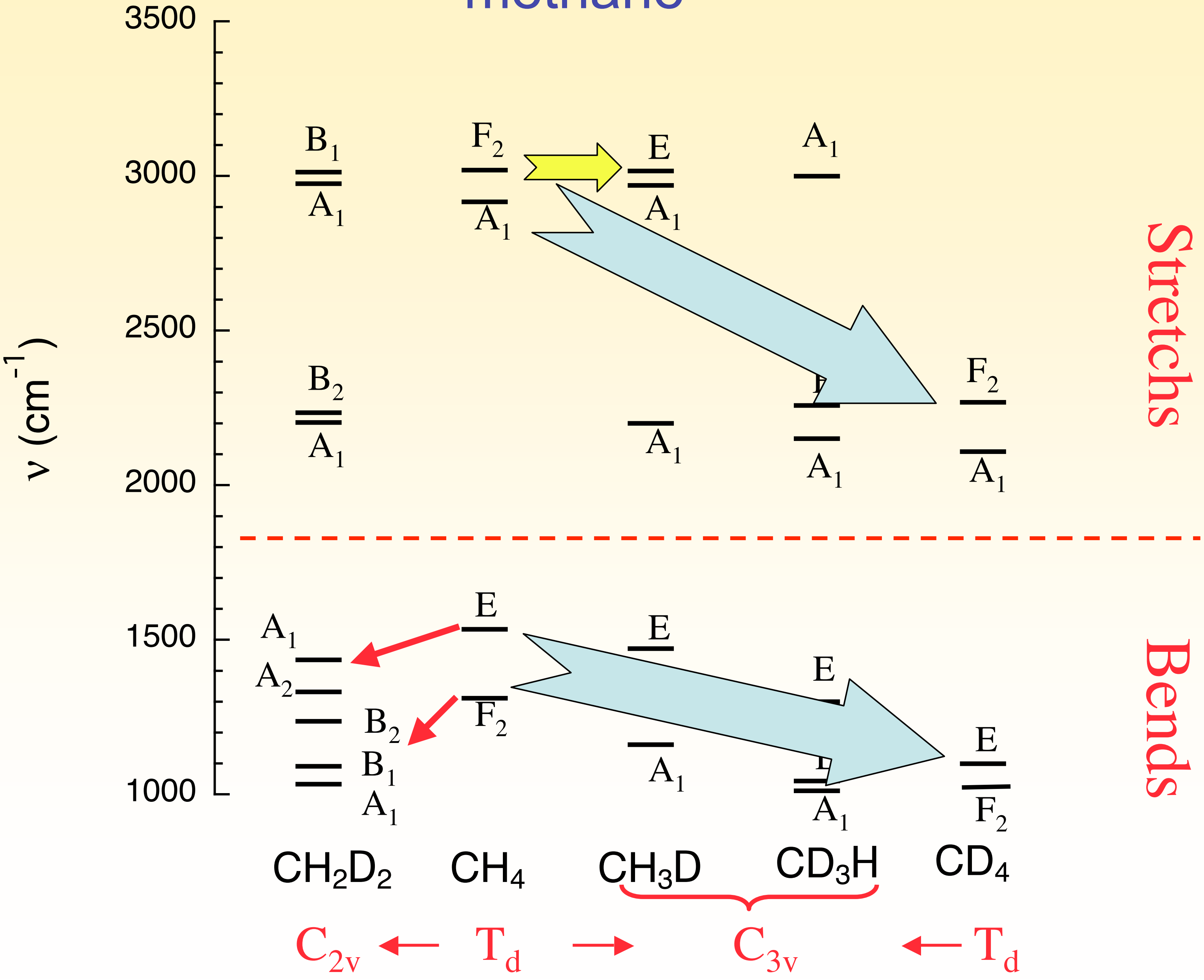
* Notation: $\{\, \{ \{1\}^{\infty} , \{3\}^{\infty} \}^{\infty} \;, \{2\}^{\infty} \,\}$

Isotopologues of methane:

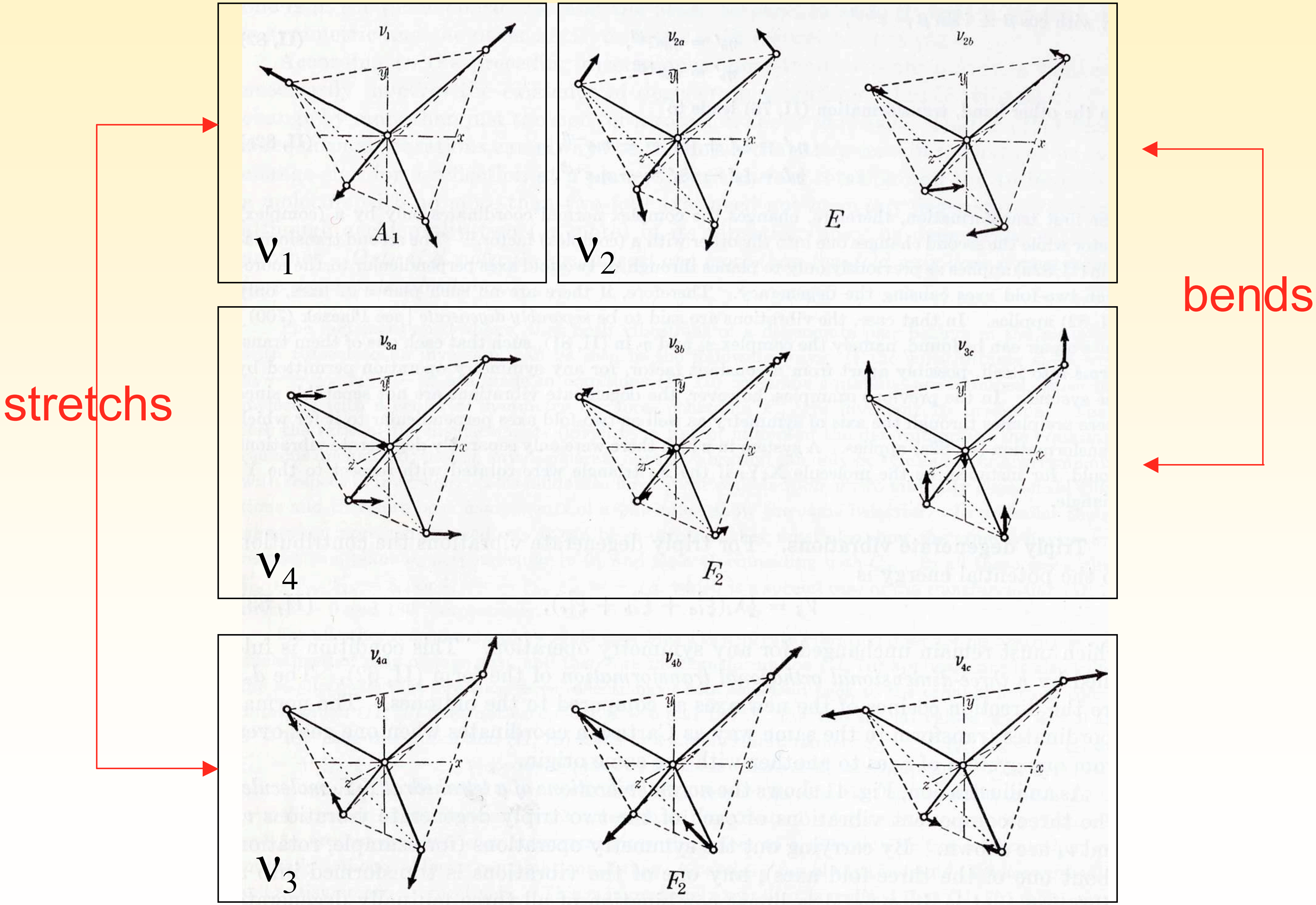
CH_4 , CD_4 , CT_4 , $^{13}CH_4$	T_d	4 modes
CH_3D , CD_3H	C_{3v}	6 modes
CH_2D_2	C_{2v}	9 modes



Fundamental frequencies of the isotopologues of methane



Methane CH_4



Best contraction scheme for CH_4

MSP step (minimal symmetry preserving step)

a_1 e f_2 f_2

$\{1\}^\infty, \{2,3\}^\infty, \{4,5,6\}^\infty, \{7,8,9\}^\infty$

10 HOs / degree of freedom

$\{\, \{1\}^\infty, \{4,5,6\}^\infty \,\}^\infty \;,\; \{2,3\}^\infty \;,\; \{7,8,9\}^\infty$

$\{\, \{\, \{1\}^\infty, \{4,5,6\}^\infty \,\}^\infty, \{2,3\}^\infty, \{7,8,9\}^\infty \,\}$

Energy truncations → δ_1 δ_2 δ_3 δ_{tot}

4000 < Final basis set size < 16000

convergence to the cm^{-1}

Assignment	irreps.	4x	40	41	exp.
ν_4	F2	1297.1	1308.9	1308.7	1310.8
ν_2	E	1519.2	1528.4	1528.2	1533.3
$2\nu_4$	A1	2570.5	2588.8	2588.9	2587.3
$2\nu_4$	F2	2585.7	2611.2	2611.0	2614.2
$2\nu_4$	E	2596.6	2622.3	2621.8	2624.6
$\nu_2 + \nu_4$	F2	2805.7	2827.0	2827.0	2838.2
$\nu_2 + \nu_4$	F1	2813.8	2838.6	2838.2	2846.0
ν_1	A1	2924.4	2925.0	2925.0	2916.5
ν_3	F2	3015.2	3027.0	3026.3	3019.5
$2\nu_2$	A1	3033.8	3051.7	3051.5	3064.4
$2\nu_2$	E	3036.5	3054.7	3054.4	3065.1
$3\nu_4$	F2	3848.0	3878.6	3878.8	3870.5
$3\nu_4$	A1	3872.8	3913.5	3913.3	3909.2
$3\nu_4$	F1	3882.3	3923.5	3923.2	3920.5
$3\nu_4$	F2	3894.7	3935.8	3935.4	3930.5
$\nu_2 + 2\nu_4$	E	4074.4	4104.8	4105.1	4105.2
$\nu_2 + 2\nu_4$	F1	4088.5	4127.7	4127.9	4128.6
$\nu_2 + 2\nu_4$	A1	4102.6	4139.0	4138.9	4133.0
$\nu_2 + 2\nu_4$	F2	4102.2	4142.4	4142.2	4142.9
$\nu_2 + 2\nu_4$	E	4110.6	4150.8	4150.5	4151.2
$\nu_2 + 2\nu_4$	A2	4116.5	4159.1	4158.3	4161.9
$\nu_1 + \nu_4$	F2	4213.1	4226.1	4225.8	4223.5
$\nu_3 + \nu_4$	F2	4290.8	4320.0	4318.4	4319.2
$\nu_3 + \nu_4$	E	4293.7	4326.1	4324.9	4322.2
[illegible]	F1	[illegible]	[illegible]	[illegible]	[illegible]

PES: Lee, Martin, Taylor (1995)
CCSD(T)

4n: quartic PES
μ truncated at order n
x: no rotational correction

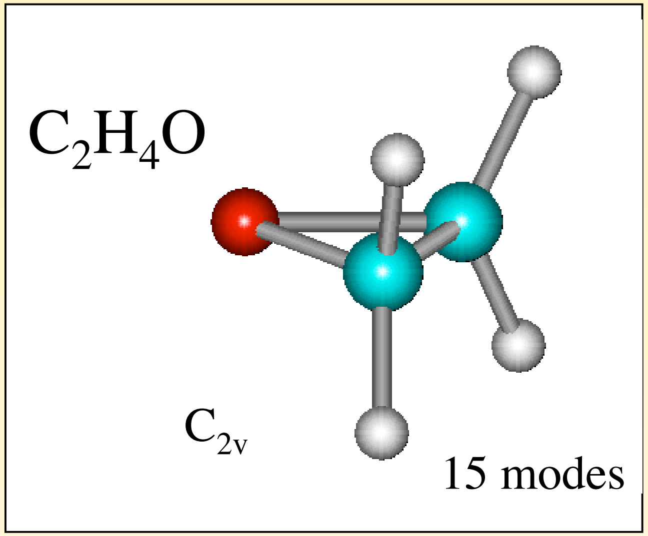
Exp: Wenger and Champion
JQSRT (1998)

Contractions with and without mean field averaging and SCF treatment

	Sym.	Harmonic level	MSP-CI	MSP-VMFCI	MSP-VSCFCI	Converged
ν_4	F2	1345	1356	1295	1318	1309
ν_2	E	1570	1567	1527	1532	1528
$2\nu_4$	A1	2691	2714	2591	2638	2588
$2\nu_4$	F2	2691	2719	2597	2643	2610
$2\nu_4$	E	2691	2719	2597	2643	2622
ν_1	A1	3036	3013	2972	2972	2925
ν_3	F2	3157	3214	3176	3062	3027
$2\nu_2$	A1	3141	3131	3051	3061	3051
$2\nu_2$	E	3141	3134	3054	3064	3054
$3\nu_4$	F2	4036	4079	3896	3966	3868
$3\nu_4$	A1	4036	4087	3905	3974	3905
$3\nu_4$	F1	4036	4088	3905	3974	3915
$3\nu_4$	F2	4036	4088	3906	3974	3929
$3\nu_2$	E	4711	4694	4579	4588	4573
$3\nu_2$	A2	4711	4699	4579	4594	4579
$3\nu_2$	A1	4711	4699	4579	4594	4579

ETHYLENE OXYDE

VMFCI solution:



Bégué, Gohaud, Pouchan, Cassam-Chenaï, Liévin . JCP (in press)

Pau: P-VMWCI method

{1}{2} ··· {15}	converged VSCF 8 cycles

{1-6-9-13} 2 {3-5-12} 4 7 8 10 11 14 15

VMFCI 1
2 cycles

CH stretches truncated at 34000 cm^{-1}

ring modes truncated at 19000 cm^{-1}

{{1-6-9-13}- {7}-{10}} 2 {3-5-12} 4 8 11 14 15

VMFCI 2
2 cycles

truncated at 19500 cm^{-1}

Full-CI

truncated at 10721 cm^{-1}

300000 basis functions

Convergence of VMFCI results

	truncated at:	VSCF/VCI 8400 cm^{-1}	VMFCI 8400 cm^{-1}	VMFCI 9200 cm^{-1}	VMFCI 10000 cm^{-1}	VMFCI 10721 cm^{-1}	exp. IR gaz phase	
	# basis functions:	(42113bf)	(46525bf)	(91052bf)	(172204bf)	(298195bf)		Assignment
A_1	ν_1	2994	2927	2921	2920	2919	3018	CH_2 s-str
	ν_2	1501	1500	1500	1497	1497	1497, 1498	CH_2 scis
	ν_3	1273	1274	1273	1271	1272	1270	Ring str
	ν_4	1128	1128	1126	1123	1123	1148	CH_2 wag
	ν_5	881	881	879	879	879	877	Ring deform
	ν_6	3093	3040	3034	3033	3032	inactive	CH_2 as-str
A_2	ν_7	1153	1153	1151	1149	1149	inactive	CH_2 twist
	ν_8	1024	1024	1020	1019	1019	1020	CH_2 rock
	ν_9	3040	2922	2915	2914	2914	3006	CH_2 s-str
B_2	ν_{10}	1473	1471	1471	1468	1468	1470, 1472	CH_2 scis
	ν_{11}	1130	1130	1128	1125	1125	1151	CH_2 wag
	ν_{12}	825	825	823	823	823	822, 840	Ring deform
	ν_{13}	3105	3052	3044	3042	3041	3065	CH_2 as-str
B_1	ν_{14}	1151	1151	1149	1147	1147	1142	CH_2 twist
	ν_{15}	801	796	794	793	794	808,821	CH_2 rock

hybrid CCSD(T)/cc-pVTZ//B3LYP/6-31+G(d,p) quartic potential

Conclusions

The VMFCI method implemented in the CONVIV code is a flexible tool for solving the vibrational problem

Taking advantage of the hierarchical contraction procedure and of the mean field treatment applied at all steps, it provides very compact wave functions

Large molecules could be calculated by defining a restricted active space of modes explicitely included in the VMFCI contractions, all spectator modes being described by the mean field