

# A new approach for calculating rotational spectra

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# Forbidden rotational lines of CH<sub>4</sub>

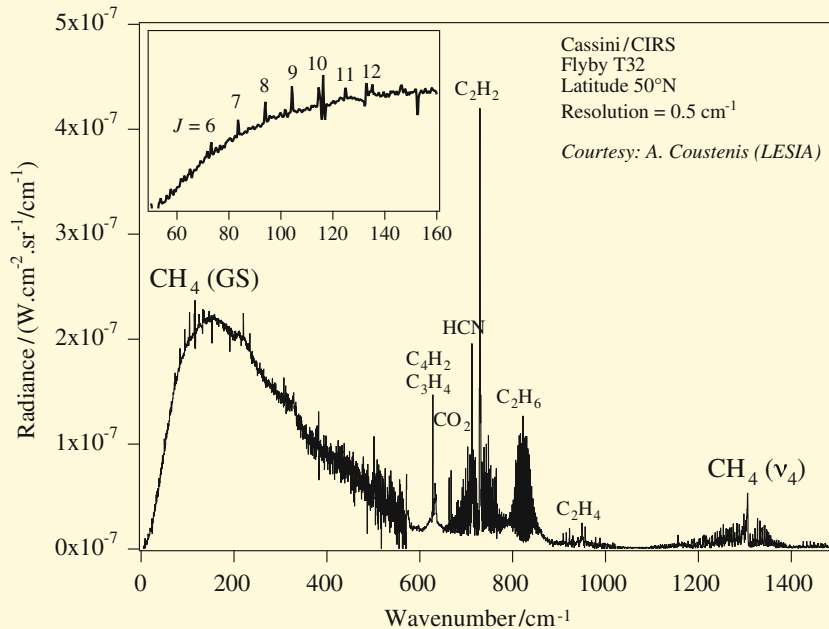


Fig. 1. Example of a Cassini CIRS spectrum showing far infrared emission lines of methane.



in Titan atmosphere (32<sup>th</sup> Cassini flyby: 950 km, 13/06/2007)

# Forbidden rotational lines of CH<sub>4</sub>

E.H. Wishnow et al. / *Journal of Quantitative Spectroscopy & Radiative Transfer* 103 (2007) 102–117

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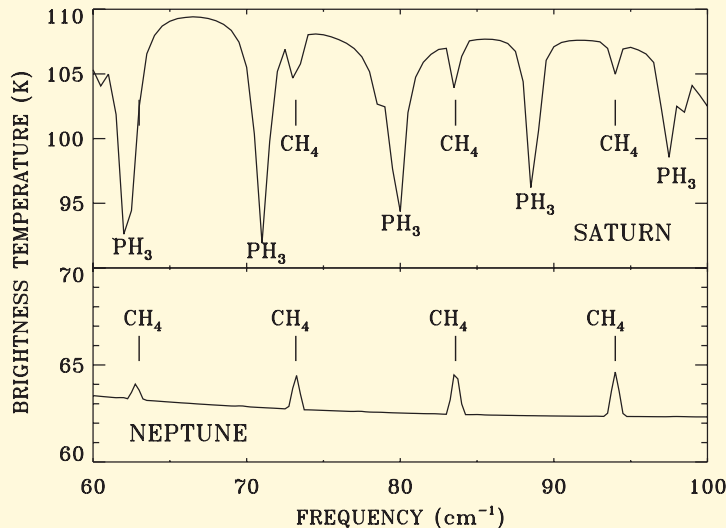


Fig. 5. *Upper panel:* synthetic spectrum of zenith radiation from Saturn at a resolution of  $0.5\text{ cm}^{-1}$ . The strongest features arise from allowed rotational transitions in  $\text{PH}_3$ . The  $\text{CH}_4$  features are distortion dipole envelopes  $R(6)$ ,  $R(7)$ , and  $R(8)$ , with  $R(5)$  being obscured by the lowest frequency phosphine line. Some very weak  $\text{NH}_3$  transitions (unlabeled) contribute as well. All these lines occur in absorption. *Lower panel:* synthetic spectrum of zenith radiation from Neptune at a resolution of  $0.5\text{ cm}^{-1}$ . The methane is abundant enough that the distortion dipole envelopes  $R(5)$  to  $R(8)$  are the strongest narrow features present. The stratosphere is sufficiently warm that these lines appear in emission on a continuum arising from collision-induced  $\text{H}_2\text{-H}_2$  and  $\text{H}_2\text{-He}$  absorption.

can be used to derive CH<sub>4</sub> abundances in Titan, Saturn and Neptune.

# Problem: electric dipole moment uncertainty

**Table 2**  
Dipole moment parameters.

Fit #	Nb. data	$\sigma$	$d_{\text{RMS}}$ (%)	$d_{\text{RMS}}^J$ (%)	$\mu_0$ ( $\mu\text{D}$ )	$\mu_D$ ( $\mu\text{D}$ )	$\mu_{2,4}$ (mD)	$\mu_{4,4}$ (mD)
1	92	1.468	8.52	3.53	7.976 (29)	22.559 (82)	–	–
2	92 (GS)	1.468	8.52	3.53	7.976 (28)	22.559 (79)	–	–
	96 (Dyad)	1.309	8.74	3.98	–	–	7.00 (13)	–36.09 (16)
3	96	1.306	8.74	3.98	7.9765 <sup>a</sup>	22.559 <sup>a</sup>	7.00 (13)	–36.09 (15)
Hilico [23]	(Calc.)	–	–	–	7.90	22.34	10.8	–34.7
Ozier [28]	(Stark)	–	–	–	–	24.06 (45)	–	–
Wishnow [25]	3 <sup>b</sup>	–	–	–	–	23.82 (88)	–	–
						23.94 (1.20)		
Ozier [41]	2	–	–	–	–	–	–	–33.8 (4.9)
Mourbat [40]	(Calc.)	–	–	–	–	–	7.186	–37.47

For fit number 2 (global fit), the two numbers correspond to the cold and hot band lines, respectively.  $d_{\text{RMS}}^J$  is the root mean square deviation for total intensities of  $J$  clusters (see text). The two  $\mu_D$  values indicated for Wishnow correspond to the so-called low- ( $0.24 \text{ cm}^{-1}$ ) and high- ( $0.06 \text{ cm}^{-1}$ ) resolution spectra from this reference.

<sup>a</sup> Fixed value.

<sup>b</sup> Unresolved clusters.

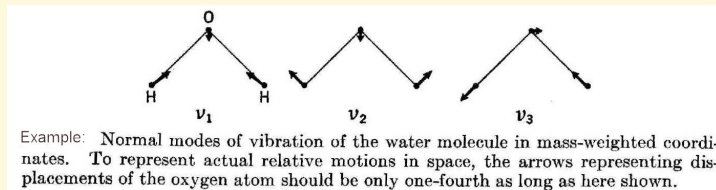
*Boudon et al. JQSRT 111, p. 1117 (2010)*

Can ab initio calculations resolve the controversy?

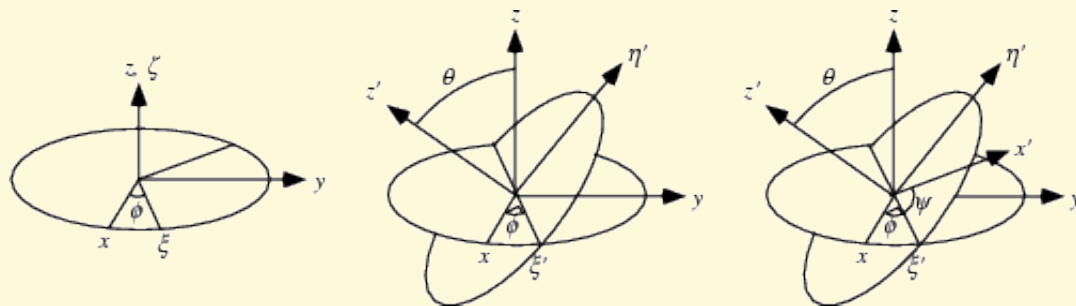
# Effective observable theory - condition 1

Two families of distinguishable degrees of freedom (dof)  $\rightsquigarrow$  two sets of operators:  $X$  and  $Y$  acting on each family respectively.

- Ex.  $X$  normal coordinates operators and conjugate moments



- Ex.  $Y$  Euler angles operators and conjugate moments



## Effective observable theory - condition 2

The Hamiltonian  $H(X, Y)$  which act on the tensor Hilbert space  $V = V_{\mathbf{X}} \otimes V_{\mathbf{Y}}$  is “dominated” by a term of the form,  $H_0(X) \otimes Id_{\mathbf{Y}}$ .

↪ Introducing  $\varepsilon$  and  $H(X, Y, \varepsilon) = H_0(X) \otimes Id_{\mathbf{Y}} + \varepsilon H_1(X, Y)$

such that  $H(X, Y, 0) = H_0(X) \otimes Id_{\mathbf{Y}}$  and  $H(X, Y, 1) = H(X, Y)$ .

↪ Given an eigenbasis for the  $\dim V_{\mathbf{Y}}$ -degenerate eigenspaces of  $H(X, Y, 0)$ ,

$$H(X, Y, 0)|\psi_n \otimes \Psi_K\rangle = \nu_n|\psi_n \otimes \Psi_K\rangle \quad \forall K.$$

We assume that, for some fixed  $n$ , the  $\dim V_{\mathbf{Y}}$  eigenstates  $(\psi_n \otimes \Psi_K)_K$  of  $H(X, Y, 0)$  are in one-to-one correspondance with  $\dim V_{\mathbf{Y}}$  eigenstates of  $H(X, Y, \varepsilon)$ , denoted by  $(\phi_{n,K}(\varepsilon))_K$ , **with a smooth  $\varepsilon$  dependency**.

# Effective wave operator

The  $\phi_{n,K}(\varepsilon)$ 's can be expanded on the tensorial product basis set as,

$$\phi_{n,K}(\varepsilon) = \sum_{n',K'} c_{n',K'}^{n,K}(\varepsilon) \psi_{n'} \otimes \Psi_{K'}.$$

Defining  $\dim V_{\mathbf{X}}$  linear operators on  $V_{\mathbf{y}}$ ,  $\Psi_{n'}(Y, \varepsilon)$ , by

$$\forall n', \forall \Psi_K, \quad \Psi_{n'}(Y, \varepsilon) \Psi_K := \sum_{K'} c_{n',K'}^{n,K}(\varepsilon) \Psi_{K'},$$

and then, a so-called "effective wave operator" from  $V_{\mathbf{y}}$  onto  $V_{\mathbf{X}} \otimes V_{\mathbf{y}}$ ,  $\phi_n(Y, \varepsilon)$ , by

$$\phi_n(Y, \varepsilon) = \sum_{n'} \psi_{n'} \otimes \Psi_{n'}(Y, \varepsilon),$$

$\phi_{n,K}(\varepsilon)$  assumes a pseudo-factored form,

$$\phi_{n,K}(\varepsilon) = \phi_n(Y, \varepsilon) \Psi_K.$$

# Effective Hamiltonians

Finding the  $\dim V_{\mathbf{y}}$  eigenpairs  $(E_{n,K}(\varepsilon), \phi_{n,K}(\varepsilon))_K$  of  $H(X, Y, \varepsilon)$  at once, amounts to finding effective operators  $\phi_n(Y, \varepsilon)$  and  $E_n(Y, \varepsilon)$  acting on  $V_{\mathbf{y}}$  such that,

$$H(X, Y, \varepsilon)\phi_n(Y, \varepsilon) = \phi_n(Y, \varepsilon)E_n(Y, \varepsilon) \quad (1)$$

$$\phi_n(Y, \varepsilon)\Psi_K = \phi_{n,K}(\varepsilon) \quad (2)$$

$$E_n(Y, \varepsilon)\Psi_K = E_{n,K}(\varepsilon)\Psi_K \quad (3)$$



# Effective Dipole Moment

For  $\varepsilon = 1$ , the Hermitic conjugate of the generalized eigenequation,

$$H(X, Y)\phi_n(Y) = \phi_n(Y)E_n(Y)$$

is,

$$\phi_n^\dagger(Y)H(X, Y) = E_n^\dagger(Y)\phi_n^\dagger(Y),$$

One derives for the laboratory-fixed, dipole moment,  $D(X, Y)$ , acting on  $V_{\mathbf{x}} \otimes V_{\mathbf{y}}$ , an effective Hermitian operator,  $D_n(Y)$ , acting solely on  $V_{\mathbf{y}}$ , by,

$$D_n(Y) = \langle \phi_n^\dagger(Y)D(X, Y)\phi_n(Y) \rangle_{\mathbf{x}}. \quad (4)$$

with the normalization condition,

$$\langle \phi_n^\dagger(Y)\phi_n(Y) \rangle_{\mathbf{x}} = Id_{\mathbf{y}}, \quad (5)$$

where the notation  $\langle \dots \rangle_{\mathbf{x}}$  means that integration is carried over the  $\mathbf{x}$ -variables only

## Watson-Eckart Hamiltonian decomposition

- $X$  normal coordinates operators and conjugate moments
- $Y$  Euler angles operators and conjugate moments

$$H_{watson}(X, Y) = H_0(X) \otimes Id_{\mathbf{y}} + H_1(X, Y)$$

$$H_0(X) = \frac{1}{2} \vec{P}^T \cdot \vec{P} + V_{BO} - \frac{1}{8} Tr(\mu) + \frac{1}{2} \vec{\pi}^T \mu \vec{\pi}$$

$$H_1(X, Y) = \sum_{\alpha\beta} \frac{1}{2} \mu_{\alpha\beta} \otimes \Pi_{\alpha} \Pi_{\beta} - \mu_{\alpha\beta} \pi_{\alpha} \otimes \Pi_{\beta}$$

$\mu$  : effective reciprocal inertial tensor,

$\vec{\pi}$  : Coriolis coupling operator,

$\vec{\Pi}$  : the total angular momentum.

## Rayleigh-Schrödinger perturbative expansion and solution

$$E(Y, \varepsilon) = \nu_0 Id_{\mathbf{y}} + \varepsilon E^{(1)}(Y) + \varepsilon^2 E^{(2)}(Y) + \varepsilon^3 E^{(3)}(Y) + \varepsilon^4 E^{(4)}(Y) + \dots,$$

$$\phi(Y, \varepsilon) = \psi_0 \otimes Id_{\mathbf{y}} + \varepsilon \phi^{(1)}(Y) + \varepsilon^2 \phi^{(2)}(Y) + \varepsilon^3 \phi^{(3)}(Y) + \varepsilon^4 \phi^{(4)}(Y) + \dots,$$

$$E^{(1)}(Y) = \langle \psi_0 \otimes Id_{\mathbf{y}} | H_1(X, Y) | \psi_0 \otimes Id_{\mathbf{y}} \rangle_{\mathbf{x}} := H_1(Y)_{0,0},$$

$$\phi^{(1)}(Y) = \sum_{k \neq 0} \psi_k \otimes \frac{H_1(Y)_{k,0}}{\nu_0 - \nu_k}$$

$$E^{(2)}(Y) = \sum_{k \neq 0} \frac{H_1(Y)_{0,k} H_1(Y)_{k,0}}{\nu_0 - \nu_k},$$

...

## Dipole moment expansion and solution

dipole moment:  $D_f(X, Y) = \sum_{\alpha=x,y,z} D_\alpha(X) \otimes \lambda_{f\alpha}(Y),$

$$D_f(Y) = D_f^{(0)}(Y) + \varepsilon D_f^{(1)}(Y) + \varepsilon^2 D_f^{(2)}(Y) + \cdots + \varepsilon^n D_f^{(n)}(Y) + \cdots,$$

- order 0

$$D_f^{(0)}(Y) = \sum_{\alpha=x,y,z} \langle \psi_0 | D_\alpha(X) | \psi_0 \rangle_{\mathbf{x}} \lambda_{f\alpha}(Y)$$

$$^{12}\text{CH}_4, \text{GS} \rightsquigarrow 0$$

- order 1

$$D_f^{(1)}(Y) = \sum_{\alpha=x,y,z} \sum_{k_1 \neq 0} \frac{\langle \psi_{k_1} | D_\alpha(X) | \psi_0 \rangle_{\mathbf{x}}}{\nu_0 - \nu_{k_1}} H_1(Y)_{0,k_1} \lambda_{f\alpha}(Y) + \frac{\langle \psi_0 | D_\alpha(X) | \psi_{k_1} \rangle_{\mathbf{x}}}{\nu_0 - \nu_{k_1}} \lambda_{f\alpha}(Y) H_1(Y)_{k_1,0}$$

$$^{12}\text{CH}_4, \text{GS} \rightsquigarrow \frac{\mu_2^{(2)}}{2} (\lambda_{fx}(\Pi_y \Pi_z + \Pi_z \Pi_y) + \lambda_{fy}(\Pi_x \Pi_z + \Pi_z \Pi_x) + \lambda_{fz}(\Pi_y \Pi_x + \Pi_x \Pi_y)) + hc$$

## Dipole moment $2^{nd}$ order correction

$$D_f^{(2)}(Y) = \sum_{\alpha=x,y,z} \left( \sum_{k_1, k_2 \neq 0} \frac{1}{(\nu_0 - \nu_{k_1})(\nu_0 - \nu_{k_2})} \left( \langle \psi_{k_1} | D_\alpha(X) | \psi_{k_2} \rangle_{\mathbf{X}} H_1(Y)_{0,k_1} \lambda_{f\alpha}(Y) H_1(Y)_{k_2,0} + \right. \right. \\ \left. \langle \psi_0 | D_\alpha(X) | \psi_{k_1} \rangle_{\mathbf{X}} \lambda_{f\alpha}(Y) H_1(Y)_{k_1,k_2} H_1(Y)_{k_2,0} + \langle \psi_{k_1} | D_\alpha(X) | \psi_0 \rangle_{\mathbf{X}} H_1(Y)_{0,k_2} H_1(Y)_{k_2,k_1} \lambda_{f\alpha}(Y) \right) - \\ \sum_{k_1 \neq 0} \frac{\langle \psi_0 | D_\alpha(X) | \psi_{k_1} \rangle_{\mathbf{X}}}{(\nu_0 - \nu_{k_1})^2} \left( \lambda_{f\alpha}(Y) H_1(Y)_{k_1,0} H_1(Y)_{0,0} + H_1(Y)_{0,0} H_1(Y)_{0,k_1} \lambda_{f\alpha}(Y) \right) - \\ \left. \frac{\langle \psi_0 | D_\alpha(X) | \psi_0 \rangle_{\mathbf{X}}}{2} \sum_{k_1 \neq 0} \frac{1}{(\nu_0 - \nu_{k_1})^2} \left( \lambda_{f\alpha}(Y) H_1(Y)_{0,k_1} H_1(Y)_{k_1,0} + H_1(Y)_{0,k_1} H_1(Y)_{k_1,0} \lambda_{f\alpha}(Y) \right) \right)$$

↪ correction to  $\mu_2^{(2)}$

↪  $\mu_2^{(4)}$  in factor of  $(\Pi_y \Pi_x + \Pi_x \Pi_y)(\Pi_x^2 + \Pi_y^2 + \Pi_z^2)$  for body fixed  $z$ -axis

↪  $\mu_4^{(4)}$  in factor of  $[(\Pi_y \Pi_x + \Pi_x \Pi_y), \Pi_z^2]_+$  for body fixed  $z$ -axis

↪ no more  $(\lambda_{fx} D_x^{body-fixed} + \lambda_{fy} D_y^{body-fixed} + \lambda_{fz} D_z^{body-fixed}) + hc$

# Speed of convergence with the order of the perturbation

Energies in  $\text{cm}^{-1}$  of methane rotational levels  
in its vibrational ground state

	Van Vleck Perturbation <sup>a</sup>			Our method <sup>b</sup>			STDS <sup>c</sup>
	ord2	ord4	ord6	ord0	ord2	ord4	
$J = 1$	10.59973	10.44174	10.44237	10.63296	10.48010	10.48008	10.481648
$J = 2$	31.79918	31.32521	31.32439	31.89887	31.43746	31.43742	31.442121
	31.79918	31.32521	31.32463	31.89887	31.43772	31.43769	31.442387
$J = 3$	63.59837	62.65041	62.64064	63.79775	62.86645	62.86635	62.875779
	63.59837	62.65041	62.64162	63.79775	62.86749	62.86742	62.876841
	63.59837	62.65041	62.64285	63.79775	62.86879	62.86877	62.878169

<sup>a</sup> X. G. Wang et E. L. Sibert, *Spectrochimica Acta A*, **58** (2002) 863. 12 force constants adjusted on experiment.

<sup>b</sup> P. Cassam-Chenaï and J. Liévin, *Int. J. Quantum Chem.* **93**, 245-264 (2003). Purely *ab initio* results.

<sup>c</sup> C. Wenger and J. P. Champion, *J. Quant. Spectrosc. Radiat. Transfer* **59**, 471-480 (1998). From an effective Hamiltonian accurate to  $10^{-5} \text{ cm}^{-1}$ .

## Energies in $cm^{-1}$ of methane rotational levels in its vibrational ground state

	Carter/Bowman <sup>a</sup>	Wang/Carrington <sup>b</sup>	Wang/Sibert <sup>c</sup>	Cassam-Chenaï/Liévin <sup>d</sup>	STDS <sup>e</sup>
$J = 1$	10.47	10.430	10.44237	10.48165	10.481648
$J = 2$	N/A	N/A	31.32439	31.44213	31.442121
	N/A	N/A	31.32463	31.44240	31.442387
$J = 3$	N/A	N/A	62.64064	62.87581	62.875779
	N/A	N/A	62.64162	62.87689	62.876841
	N/A	N/A	62.64285	62.87824	62.878169
$J = 4 - 18$	N/A	N/A	N/A	largest relative difference $2.10^{-5}$	

<sup>a</sup> S. Carter et J. M. Bowman, J. Phys. Chem. **A104**, 2355 (2000). MULTIMODE using Lee, Martin and Taylor PES.

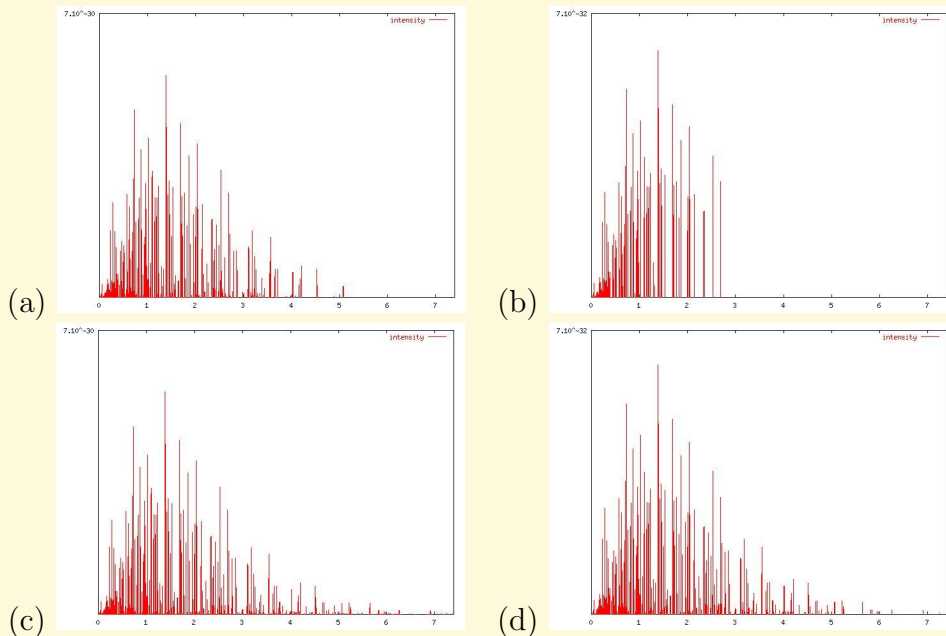
<sup>b</sup> X. G. Wang et T. Carrington, J. Chem. Phys **121**, 2937 (2004). CI calculation using Schwenke PES.

<sup>c</sup> X. G. Wang et E. L. Sibert, Spectrochimica Acta A **58**, 863 (2002). **12 force constants adjusted on experiment** .

<sup>d</sup> P. Cassam-Chenaï and J. Liévin, Int. J. Quantum Chem. **93**, 245-264 (2003). VMFCI using Lee, Martin and Taylor PES + generalised perturbation with **1 parameter  $B_0$  scaled by a factor 1.0002535** .

<sup>e</sup> C. Wenger and J. P. Champion, J. Quant. Spectrosc. Radiat. Transfer **59**, 471-480 (1998). From an effective Hamiltonian accurate to  $10^{-5} cm^{-1}$  .

# Comparison with HITRAN at 500K



**Q-Branch of the vibrational ground state of methane** . Comparison of the extrapolation from HITRAN for  $^{12}\text{CH}_4$  (a) and  $^{13}\text{CH}_4$  (b) with *ab initio* calculated spectra for  $^{12}\text{CH}_4$  (c) and  $^{13}\text{CH}_4$  (d). Units as in HITRAN, intensities in [ $\text{cm}^{-1} / (\text{molecule} \cdot \text{cm}^{-2})$ ], wave numbers in  $\text{cm}^{-1}$  . Isotopic abundances: 0.988274 for  $^{12}\text{CH}_4$ , 0.0111031 for  $^{13}\text{CH}_4$  .

**R-Branch:**  $\rightsquigarrow$  average relative error of  $2 \cdot 10^{-5}$  on line positions up to  $J=14$



## Convergence of the equilibrium CH distance of methane and electric dipole moment first derivatives with orbital basis set

Method	$r_e$ (in $\rho A$ )	$\frac{\partial \mu_z}{\partial q_{3z}}$ (in au)	$\frac{\partial \mu_z}{\partial q_{4z}}$ (in au)
MRCI/VQZ	1.08826	-0.00358(1)	+0.00233(5)
MRCI/ACVQZ	1.08690	-0.00357(65)	+0.00230(4)
MRCI/ACV5Z	1.08635	-0.00355(46)	+0.00232(0)
MRCI/ACV6Z	1.08624	-0.00354(38)	+0.00233(26)

The derivatives are with respect to the mass-weighted, Cartesian, normal coordinates of the force field of Lee, Martin and Taylor. MRCI calculations with **frozen core** for the VQZ basis set and **full core** excitations for the ACVnZ basis sets. The CI space for the ACV6Z calculation is spanned by about 16 Million CSFs.

## Dipole moment derivatives of $^{12}\text{CH}_4$ (in Debye) (adimensional normal coordinates)

Ref.	This work	Loete (1988)	Mourbat (1998)
$\frac{\partial \mu_z}{\partial q_{3z}}$	-0.074875	-0.07561(4)	-0.0754(17)
$\frac{\partial \mu_z}{\partial q_{4z}}$	+0.0750256	+0.07950(8)	+0.0808(16)
$\frac{\partial^2 \mu_z}{\partial q_1 \partial q_{3z}}$	-0.00920	N/A	-0.0009(01)
$\frac{\partial^2 \mu_z}{\partial q_1 \partial q_{4z}}$	-0.01528	-0.01657	-0.0145(12)
$\frac{\partial^2 \mu_z}{\partial q_{2a} \partial q_{3z}}$	-0.00743	-0.00800	-0.0080(03)
$\frac{\partial^2 \mu_z}{\partial q_{2a} \partial q_{4z}}$	+0.00880	+0.01286	+0.0060(09)
$\frac{\partial^2 \mu_z}{\partial q_{3x} \partial q_{3y}}$	-0.01620	N/A	-0.0310(15)
$\frac{\partial^2 \mu_z}{\partial q_{3x} \partial q_{4y}}$	-0.01568	-0.01611	-0.0163(06)
$\frac{\partial^2 \mu_z}{\partial q_{4x} \partial q_{4y}}$	+0.02583	+0.02736	+0.0337(09)

“This work” corresponds to an ACV6Z/MRCI full core dipole moment calculation for first derivatives, a VQZ/MRCI frozen core calculation for second derivatives.

## Convergence of $\mu_2^{(2)}$ ( $\mu\mathbf{D}$ ) for $^{12}\text{CH}_4$

VBF	Perturb order	1st derivatives (VQZ)	+ 2nd derivatives (VQZ)
1206	1	22.73	22.28
VBF	Perturb order	1st derivatives (ACV6Z)	+ 2nd derivatives (VQZ)
1206	1	22.60	22.15
4101	1	N/A	22.15

VBF: number of vibrational zero<sup>th</sup> order eigenfunctions used in the perturbation formulas. The 1206 (resp. 4101) functions were obtained by a VMFCI with a final CI of 4935 functions (truncation at 12225.0cm<sup>-1</sup>) (resp. 52096 functions (truncation at 18349.0cm<sup>-1</sup>)).

## Effective dipole moment parameters of $^{12}\text{CH}_4$

	VQZ/2nd order	Hilico (1987)	Boudon (2010)	Wishnow (2007)
$\mu_2^{(2)}$ ( $\mu\text{D}$ )	22.30	22.34	22.56	23.94/23.82
$\mu_2^{(4)}$ (nD)	-1.15	N/A	N/A	N/A
$\mu_4^{(4)}$ (nD)	+2.31	N/A	N/A	N/A

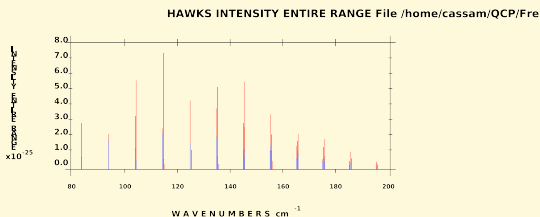
## Partition function of $^{12}\text{CH}_4$ at 296K

	this work	(McDowell) Hitran	(Wenger) Dijon <sup>a</sup>
GS only	586.959		
GS + dyad ord1	590.602		
GS + dyad ord2	590.652		
GS scaled + dyad ord2	590.427	590.4	590.5

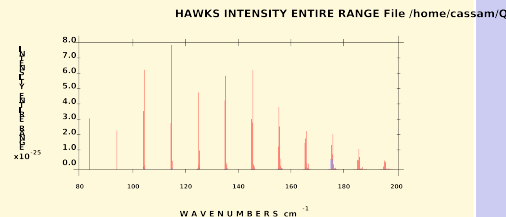
<sup>a</sup> <http://icb.u-bourgogne.fr/JSP/TIPS.jsp>

# R(7) - R(18) Comparison with SOLEIL

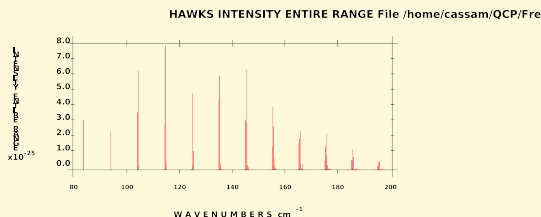
(a) Soleil



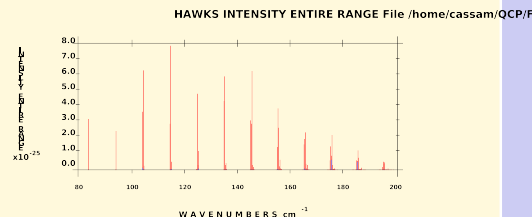
(b) hitran08



(c) ord1



(d) ord2



Average relative error after global scaling with respect to the 93 transitions reported in the Soleil experiment: ord1: 6.55%; ord2 6.32%

# The Mean Field Configuration Interaction method

$$H = \sum_{i_1} h_1(Q_{i_1}, P_{i_1}) + \sum_{i_1, i_2} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_n(Q_1, P_1, Q_2, P_2, \cdots, Q_n, P_n)$$

Consider a partition of the  $n$  degrees-of-freedom (dof) into  $q$  sets  $I_1, I_2, \cdots, I_q$ , of respectively  $p_1, p_2, \cdots, p_q$  dof,

$$(I_1, I_2, \cdots, I_q) = (\{i_1^1, i_2^1, \cdots, i_{p_1}^1\}, \{i_1^2, i_2^2, \cdots, i_{p_2}^2\}, \cdots, \{i_1^q, i_2^q, \cdots, i_{p_q}^q\}).$$

For each contraction,  $I_j$ , we define a partial Hamiltonian,

$$H_j = \sum_{i_1 \in I_j} h_1(Q_{i_1}, P_{i_1}) + \sum_{\{i_1, i_2\} \subset I_j} h_2(Q_{i_1}, P_{i_1}, Q_{i_2}, P_{i_2}) + \cdots + h_{p_j}(Q_{i_1^j}, P_{i_1^j}, Q_{i_2^j}, P_{i_2^j}, \cdots, Q_{i_{p_j}^j}, P_{i_{p_j}^j}),$$

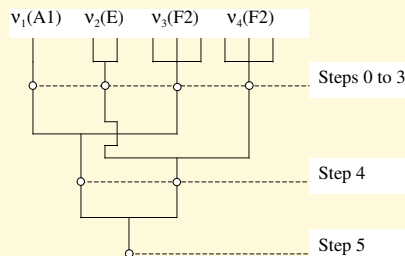
The mean-field equation for  $I_j$  is :

$$[H_j + \langle \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) | H - H_j | \prod_{I_k \neq I_j} \phi_{V_k}(Q_{i_1^k}, \cdots, Q_{i_{p_k}^k}) \rangle - \epsilon_j] \Phi_j = 0$$

## Particular cases

- The partition,  $(\{1\}, \{2\}, \dots, \{n\})$ , corresponds to the VSCF method.
- The partition,  $(\{1, 2, \dots, n\})$ , corresponds to the VCI method.

## General case: example $CH_4$





# Artefactual symmetry breaking in VSCF-based methods

Table 3

Low lying vibrational levels of methane, calculated using SPECTRO and MULTIMODE, and compared with experiment

Symmetry	Level	SPECTRO	MM-T	MM-M	Expt. [15]
A <sub>1</sub>	<i>zpe</i>	9625.83	9635.61	9633.45	
	<i>v</i> <sub>4</sub> ( <i>T</i> )	1304.24	1297.97	1298.13	1310.76
	<i>v</i> <sub>2</sub> ( <i>E</i> )	1523.49	1518.77	1518.84	1533.33
	2 <i>v</i> <sub>4</sub>	2599.73	2570.62	2568.16	2587.04
	2 <i>v</i> <sub>4</sub> ( <i>T</i> )	2600.17	2595.21	2594.81	2614.26
	2 <i>v</i> <sub>4</sub> ( <i>E</i> )	2600.21	2601.91	2601.93	2624.62
	<i>v</i> <sub>1</sub>	2902.58	2915.33	2907.31	2916.48
	<i>v</i> <sub>3</sub> ( <i>T</i> )	2997.64	3013.25	3008.70	3019.49
	2 <i>v</i> <sub>2</sub>	3047.73	3034.38	3034.68	3063.65
	2 <i>v</i> <sub>2</sub> ( <i>E</i> )	3053.93	3041.10	3041.19	3065.14
	2 <i>v</i> <sub>1</sub>	5781.65	5811.47	5781.59	5790.00
	2 <i>v</i> <sub>3</sub>	5936.79	5995.14	5985.21	5968.10
	2 <i>v</i> <sub>3</sub> ( <i>T</i> )	5936.99	6038.48	6013.33	6004.60
	2 <i>v</i> <sub>3</sub> ( <i>E</i> )	5966.74	6042.67	6032.57	6043.80
B <sub>2</sub>	<i>v</i> <sub>4</sub> ( <i>T</i> )	1306.33	1300.33	1300.43	1310.76
	<i>v</i> <sub>3</sub> ( <i>T</i> )	2998.51	3021.15	3016.64	3019.49
B <sub>1</sub>	<i>v</i> <sub>4</sub> ( <i>T</i> )	1306.31	1300.39	1300.49	1310.76
	<i>v</i> <sub>3</sub> ( <i>T</i> )	2998.61	3021.23	3016.59	3019.49
A <sub>2</sub>	<i>v</i> <sub>2</sub> ( <i>E</i> )	1525.83	1521.31	1521.33	1533.33

The calculations using MULTIMODE involve two distinct potentials: (i) Taylor expansion (MM-T) of the normal coordinates; (ii) Morse-like expansion (MM-M) of symmetric normal coordinates. Experimental values are included to demonstrate the good prediction of MM-M for the splitting of the overtones. The overtones from SPECTRO are not reliable (see text).

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# VMFCI Convergence with the number of iterations

Minimal symmetry preserving contraction scheme:  
 $\{1\}^{n+1}, \{2, 3\}^{n+1}, \{4, 5, 6\}^{n+1}, \{7, 8, 9\}^{n+1}$ , where  $n$  is the step number

		Step 0	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
$CMu_4$	$\nu_1$	8607.17	8562.01	8610.13	8599.51	8604.15	8602.97	8603.43
	$\nu_2$	4301.54	4346.44	4303.40	4308.75	4304.61	4305.25	4304.85
	$\nu_3$	9269.15	8434.91	8502.39	8430.60	8439.83	8433.05	8434.18
	$\nu_4$	3279.51	3465.49	3407.24	3424.15	3418.05	3419.79	3419.17
$CH_4$	$\nu_1$	297 2.15	297 1.39	2972 .30	2972.2 1	2972.24	2972.24	2972.24
	$\nu_2$	152 7.48	153 4.05	1532 .21	1532 .47	1532.4 0	1532.41	1532.41
	$\nu_3$	3 176.01	30 62.09	30 65.73	3061 .53	3061 .74	3061.5 8	3061.60
	$\nu_4$	12 95.15	132 0.08	131 7.25	1318 .18	1318.0 6	1318.1 0	1318.09
$CD_4$	$\nu_1$	2113.93	2113.72	2114.00	2113.98	2113.98	2113.98	2113.98
	$\nu_2$	1088.49	1091.96	1091.26	1091.36	1091.34	1091.35	1091.34
	$\nu_3$	2343.19	2280.99	2282.47	2280.73	2280.80	2280.75	2280.75
	$\nu_4$	989.36	1003.08	1001.93	1002.32	1002.28	1002.29	1002.29
$CT_4$	$\nu_1$	1731.74	1731.65	1731.79	1731.78	1731.78	1731.78	1731.78
	$\nu_2$	892.24	894.65	894.24	894.30	894.29	894.29	894.29
	$\nu_3$	1996.59	1952.17	1953.05	1952.00	1952.04	1952.01	1952.01
	$\nu_4$	851.69	861.39	860.70	860.93	860.91	860.91	860.91

A basis set of 10 HO has been used for each degree of vibration, with no truncation. The degree of vibration labelled by 1, corresponds to the vibrational mode  $\nu_1$ , those labelled by 2 and 3 to the doubly degenerate mode  $\nu_2$ , 4, 5, 6 and 7, 8, 9, to the triply degenerate modes  $\nu_3$  and  $\nu_4$ , respectively

# VMFCI versus traditional contractions

	Harmonic level	MSP-CI	MSP-VMFCI	MSP-VSCFCI	Converged
$\nu_4$	1345	1356	1295	1318	1309
$\nu_2$	1570	1567	1527	1532	1528
$2\nu_4$	2691	2714	2591	2638	2588
$2\nu_4$	2691	2719	2597	2643	2610
$2\nu_4$	2691	2719	2597	2643	2622
$\nu_1$	3036	3013	2972	2972	2925
$\nu_3$	3157	3214	3176	3062	3027
$2\nu_2$	3141	3131	3051	3061	3051
$2\nu_2$	3141	3134	3054	3064	3054
$3\nu_4$	4036	4079	3896	3966	3868
$3\nu_4$	4036	4087	3905	3974	3905
$3\nu_4$	4036	4088	3905	3974	3915
$3\nu_4$	4036	4088	3906	3974	3929
$3\nu_2$	4711	4694	4573	4588	4573
$3\nu_2$	4711	4699	4579	4594	4579
$3\nu_2$	4711	4699	4579	4594	4579

Wave numbers in  $cm^{-1}$  of the vibrational levels of methane calculated for different MSP-methods. MSP-CI goes in the wrong direction for modes 3 and 4 MSP-VSCFCI always go in the right direction and modes 1 and 2 are closer to the converged value than with MSP-CI. (HO modal basis set with quantum number less than 10. Order 0 rotational corrections).

# ZPE Convergence in CH<sub>4</sub> VMFCI scheme

step type	ZPE in cm <sup>-1</sup> (nb. bf)			
	$\nu_1$ (10 bf)	$\nu_3$ (220 bf)	$\nu_2$ (120 bf)	$\nu_4$ (680 bf)
MSP-VMFCI	97 36.817797	9 817.832496	9 830.213859	9 828.829953
MSP-VMFCI	972 4.937053	9721 .80854	972 4.971052	972 4.624952
MSP-VMFCI	9721.4 92681	9721 .614393	9721 .617023	9721 .613361
MSP-VMFCI	9721.4 94016	9721.489 747	9721.4 94231	9721.4 93759
MSP-VMFCI	9721.4893 35	9721.489 504	9721.489 515	9721.489 508
MSP-VMFCI	9721.4893 34	9721.48932 8	9721.4893 35	9721.4893 34
MSP-VMFCI	9721.489327	9721.489327	9721.489327	9721.489327
VMFCI( $\nu_1 - \nu_3$ ;48000)	9704.716 970 (1781 bf)		97 21.489327	97 21.489327
VMFCI( $\nu_1 - \nu_3$ ;22000)	9704.716 970 (330 bf)		9704.716 867	9704.716 590
VCI(18349)		9698.84 1643 (52096 bf)		

179,520,000 HO product basis functions at step 0.

## Effective observable theory - open problems

↪ Radius of convergence :

$$R = \frac{\inf(\nu_n - \nu_{n-1}, \nu_{n+1} - \nu_n)}{\sup_{\alpha, \beta}(\mu_{\alpha, \beta})} \quad ?$$

↪ Speed of convergence:

what accuracy can be expected on energy levels and wave functions as a function of  $1/R$  and perturbation order ?

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