

COMPUTATIONAL TOOLS FOR HIGH-RESOLUTION MOLECULAR SPECTROSCOPY

Attila G. Császár

Laboratory of Molecular Spectroscopy
Institute of Chemistry
Eötvös University
Budapest, Hungary



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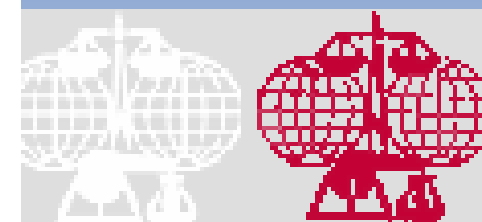
ERA-Chemistry

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QUAntitative Spectroscopy
for Atmospheric and
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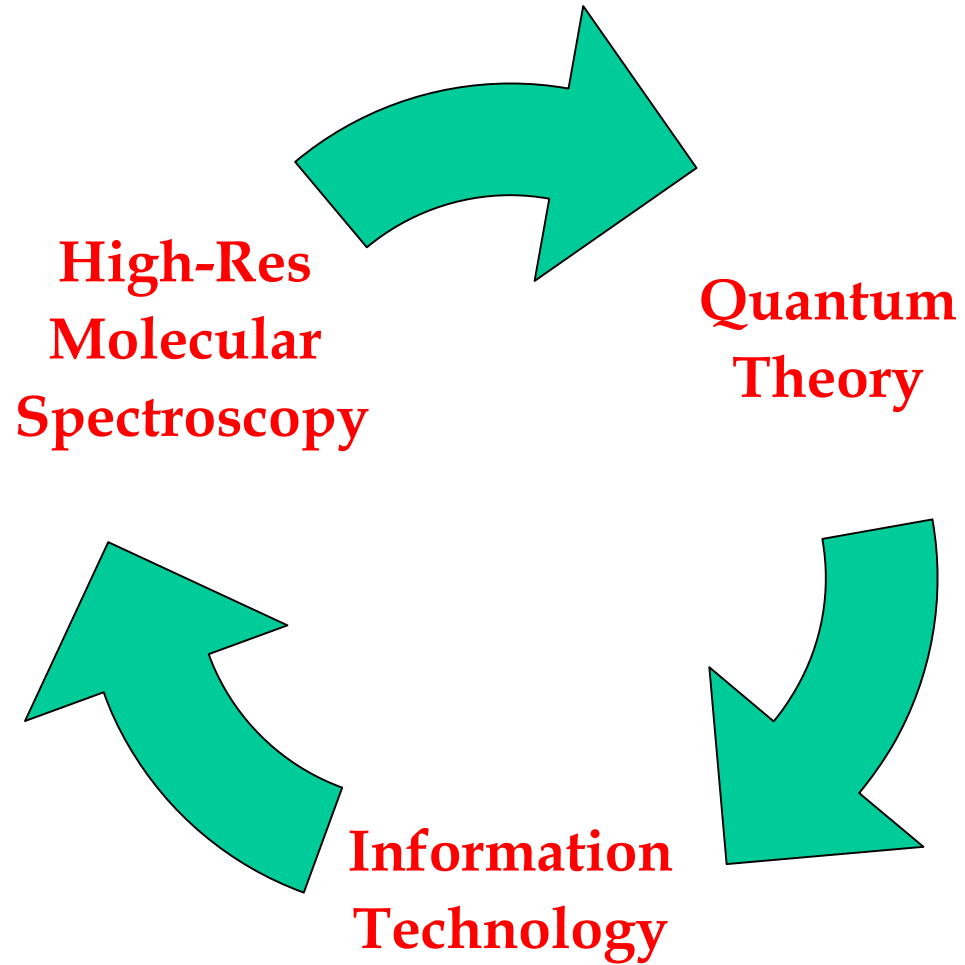
National Science Foundation
WHERE DISCOVERIES BEGIN

COST

OUTLINE

- **Introduction**
- **MARVEL: a Hamiltonian-free approach to molecular spectroscopy**
- **First-principles methods to compute rovibrational spectra (as well as quantum reaction kinetics and molecular dynamics)**
- **Summary and outlook**

Spectropedia



Quantum Mechanics

- Quantum particles, nuclei and electrons, vs. atoms and molecules
- Full treatment is still impractical for chemistry for all but the simplest many-body systems
- Often it is sufficient to solve the time-independent Schrödinger equation (TISE)
- Introduction of the Born-Oppenheimer (BO) approximation results in electronic structure and nuclear motion theories
- No practical analytic solutions: variational and perturbative treatments

$$\mathbf{H} = (\mathbf{T} + \mathbf{V}) = \mathbf{E}$$

Electronic structure

Nuclear motion

Coordinates	Cartesian	Different internals
Kinetic energy	Simple form	Complex form
Potential energy	Known exactly	Unknown (PES)
Basis set	Consensus (GTO)	No consensus
Representation	FBR	VBR, FBR, DVR
# of Eigenvalues	One or a few	(Very) many
Diagonalization	Davidson	Lanczos(?)
Approximations	PT + VAR	PT + VAR

**Rovibrational molecular
spectroscopy:**

the traditional experimental paradigm
for precision and accuracy

**First-principles variational
molecular spectroscopy:**

a new computational paradigm
for precision and accuracy

Why measure (bound) molecular states (spectra) of molecules?

- Modeling in many scientific and engineering applications (*e.g.*, star formation models, atmospheric modeling, including the greenhouse effect, and combustion) need detailed, precise, T -dependent, line-by-line information, usually deposited in old-fashioned databases (information systems)
- Most detailed information about the structure and dynamics of molecules and their motion
- Resonances and tunneling are also of great recent interest, partly for reaction dynamics

Why compute (bound) molecular states (spectra) of molecules?

- Provide tests for theoretical as well as experimental methods (including testing of potential energy (PES) and dipole moment (DMS) hypersurfaces)
- Combine theory and experiment to obtain the maximum information for spectra of molecular systems
- Unravel complicated experimental spectra
- Make predictions for experimentally not easily accessible or unaccessible spectral regions or features
- Bridge equilibrium and effective molecular properties
- Provide bridge between (overtone) spectroscopy (anharmonicity and resonances) and dynamics (*e.g.*, IVR, vibrational adiabaticity, quantum ergodicity)

Electronic structure calculations



Potential energy (hyper)surface (**PES**) [energies (and derivatives) over a grid] Property (*e.g.*, dipole) surface (**DMS**) over a grid

Nuclear motion calculations



Energy levels, wave functions, and expectation values, including dipole transition moments



SPECTRA

Spectroscopic databases



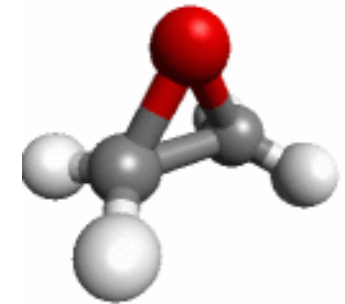
High-resolution
Transmission
Molecular
Absorption
Database
(Harvard-
Smithsonian)



Atmospheric
Radiation
Analysis
(GEISA)



Quantitative
Infrared
Database
(NIST)



Cologne
Database for
Molecular
Spectroscopy
(CDMS)

MARVEL: An inverse, Hamiltonian-free approach to highly accurate rovibrational energy levels



**Measured Active
Rotational-Vibrational
Energy Levels**

A. G. Császár, G. Czakó, T. Furtenbacher, E. Mátyus, *Ann. Rep. Comp. Chem.* **3**, 155 (2007).
T. Furtenbacher, A. G. Császár, J. Tennyson, *J. Mol. Spectrosc.* **245**, 115 (2007)

Database of observed transition wavenumbers ν_{ij} with assignments and uncertainties

The ν_{ij} are determined by term values E_i, E_j, \dots

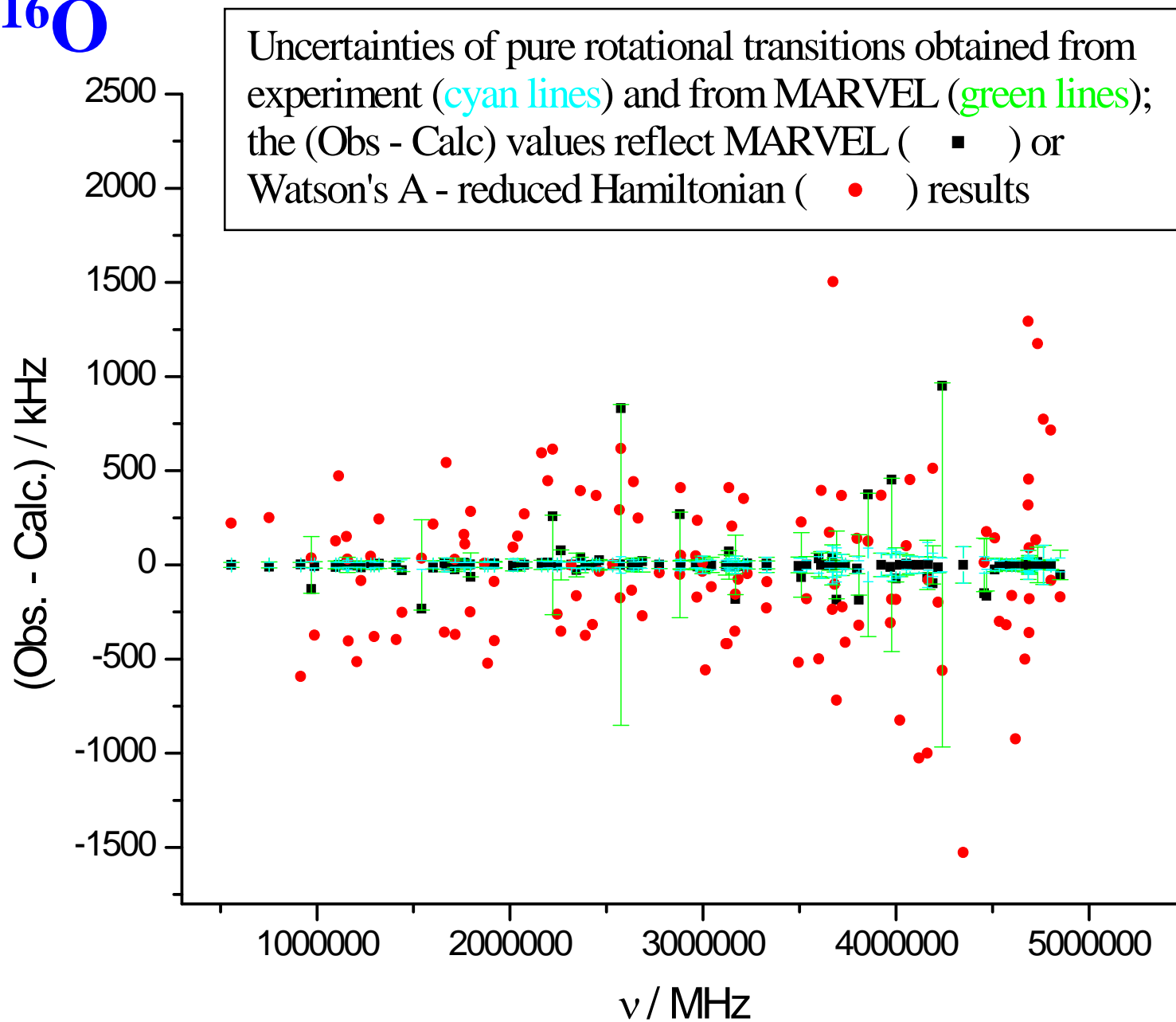
The diagram illustrates the relationship between observed transition wavenumbers, assignments, and term values. It shows a matrix equation:

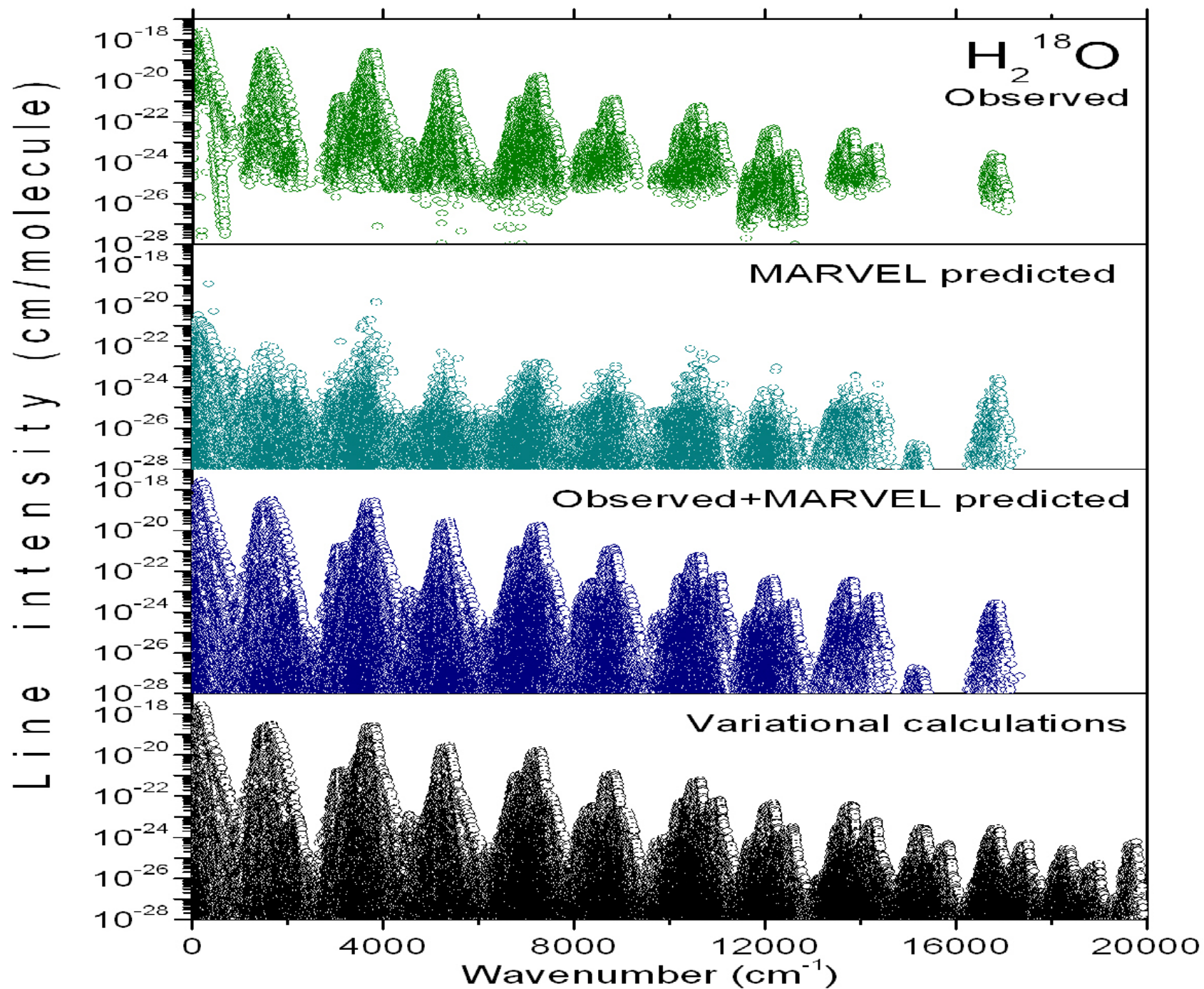
$$\mathbf{v} = \mathbf{a} \times \mathbf{E}$$

where \mathbf{v} is a matrix of observed transition wavenumbers ν_{ij} with assignments i, j in the first column. The matrix \mathbf{a} contains coefficients $+1, -1, \dots$ that determine the contribution of each term value E_i, E_j, \dots to the transition wavenumber. The vector \mathbf{E} contains the term values E_i, E_j, \dots .

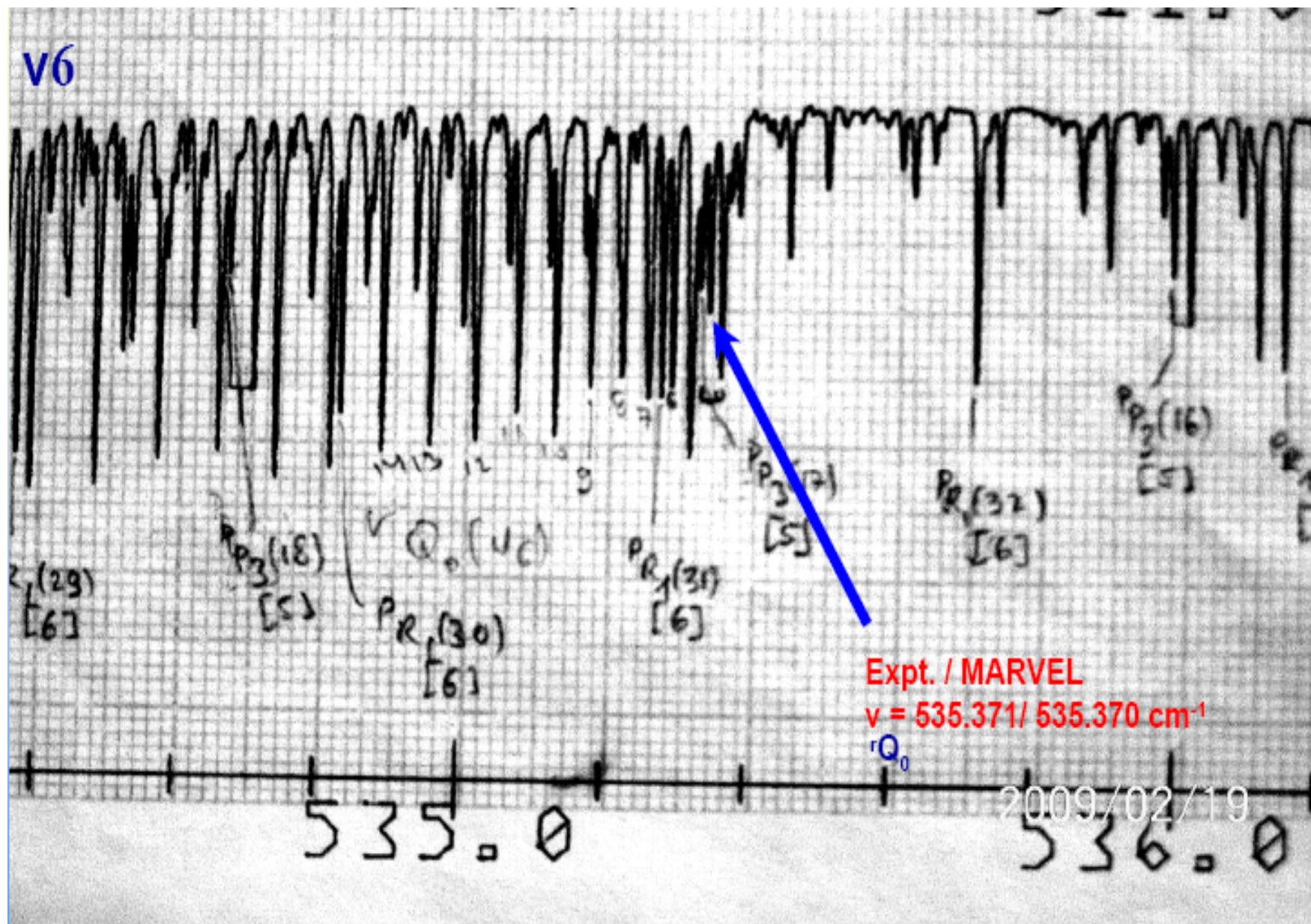
Solve for \mathbf{E} (in a least-squares sense, taking into account the experimental uncertainties of the ν_{ij}) to obtain experimentally derived term values E_i, E_j, \dots

H₂¹⁶O





Rotational-vibrational spectroscopy of ketene



**Challenge #1:
Generation of PESs from
electronic structure calculations
with an accuracy better than 10 cm^{-1}**

**Solution #1:
Focal-Point Analysis
(FPA) approach**

W. D. Allen, A. L. L. East, A. G. Császár, *Structures and Conformations of Nonrigid Molecules*, Kluwer: Dordrecht, 1993, p. 343.
A. G. Császár, W. D. Allen, H. F. Schaefer, *J. Chem. Phys.* **108**, 9751 (1998).

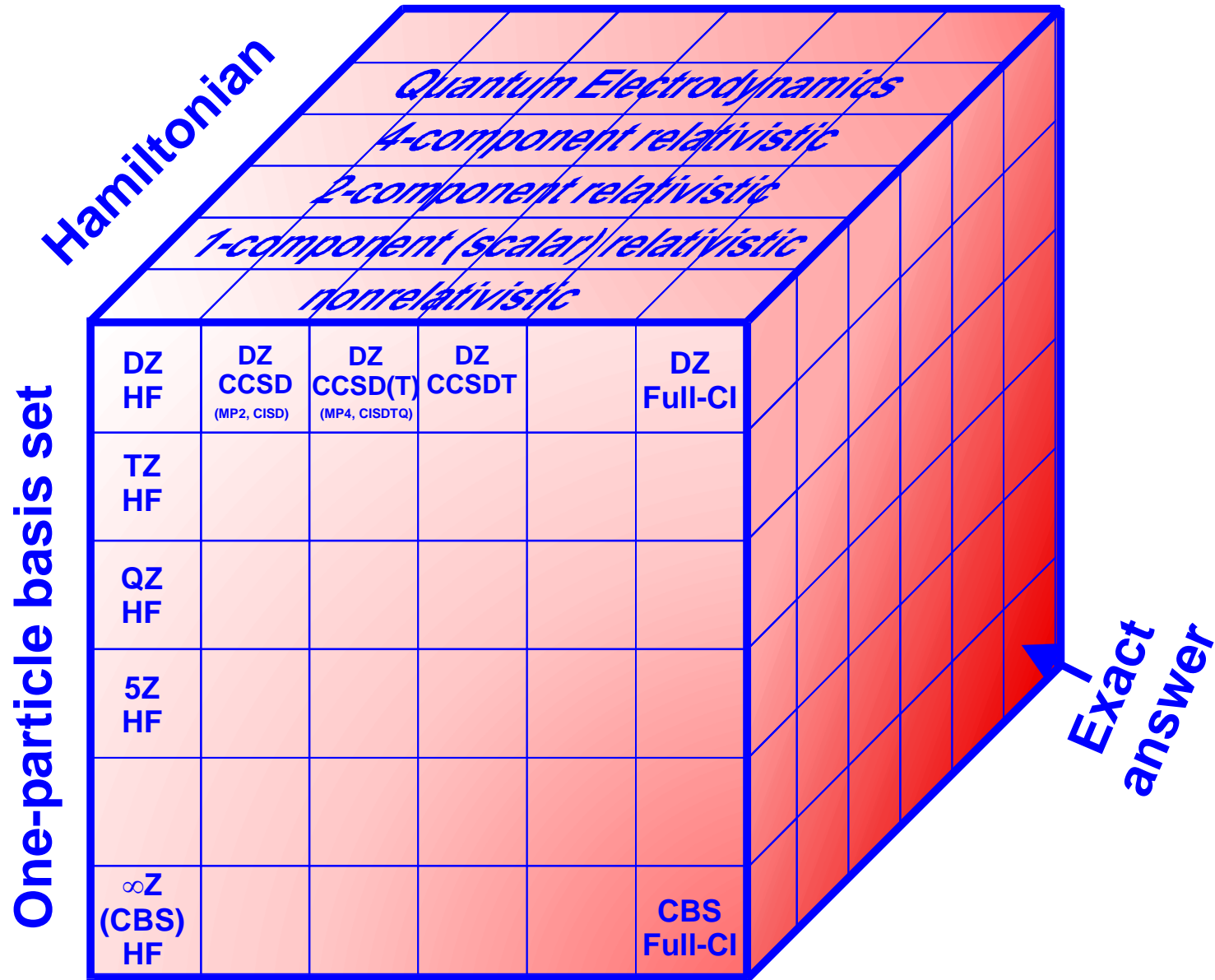
Motivations of the Focal-Point Analysis (FPA) Approach

- Get the **right result** for the **right reason** for polyatomic and polyelectronic systems.
- Attach **error bars** to theoretical predictions.
- Consider small **physical effects** tacitly neglected in most quantum chemical studies, such as core correlation, relativistic effects, and corrections to the Born-Oppenheimer approximation.
- Approach **spectroscopic accuracy** (1 cm^{-1}) as opposed to chemical (1 kcal mol^{-1}) or calibration (1 kJ mol^{-1}) accuracy in predictions of spectra.

Focal-Point Analysis (FPA) approach

- use of a family of basis sets which systematically approach completeness (*e.g.*, (aug-)cc-p(C)VnZ)
- applications of low levels of theory with prodigious basis sets (typically direct (R)HF and CASSCF computations with up to a thousand basis functions)
- higher-order (valence) correlation (HOC) treatments [these days FCI, CCSDTQ, CCSDT, CCSD(T), and (IC)MRCI] with the largest possible basis sets
- layout of a two-dimensional extrapolation grid based on an assumed additivity of correlation increments
- eschewal of empirical corrections/extrapolations
- addition of “small” correction terms (CC, Rel, DBOC)

Electron correlation treatment



Accuracy goals in electronic structure calculations

	atomic units	kJ mol ⁻¹	cm ⁻¹
Chemical accuracy	$\approx 1 \text{ m}E_h$	4	
Calibration accuracy	$\approx 0.2 \text{ m}E_h$	1	≈ 100
Spectroscopic accuracy	$\approx 1 \text{ } \mu E_h$		1
Hyperfine accuracy	$\approx 1 \text{ n}E_h$		

NB1: Obviously, it is much harder to achieve these accuracy goals in absolute energies than in relative energies chemists are mostly interested in.

NB2: These accuracies are characteristic of theoretical treatments, they have nothing to do with accuracies related to spectroscopic measurements.

Incremental buildup of the CVRQD PES of water

Valence-only problem

nearly complete basis set (extrapolated) ICMRCI

Core-correlation correction

Relativistic corrections

one-electron mass-velocity and Darwin (MVD1)

two-electron Darwin (D2)

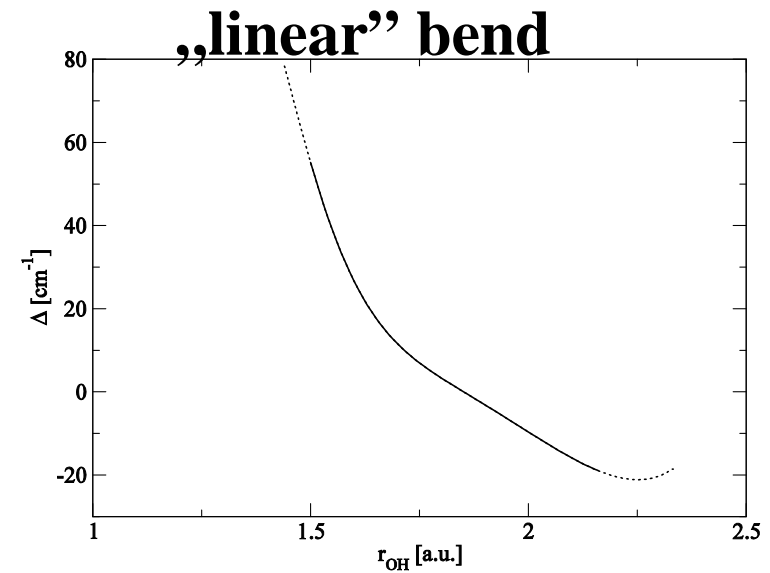
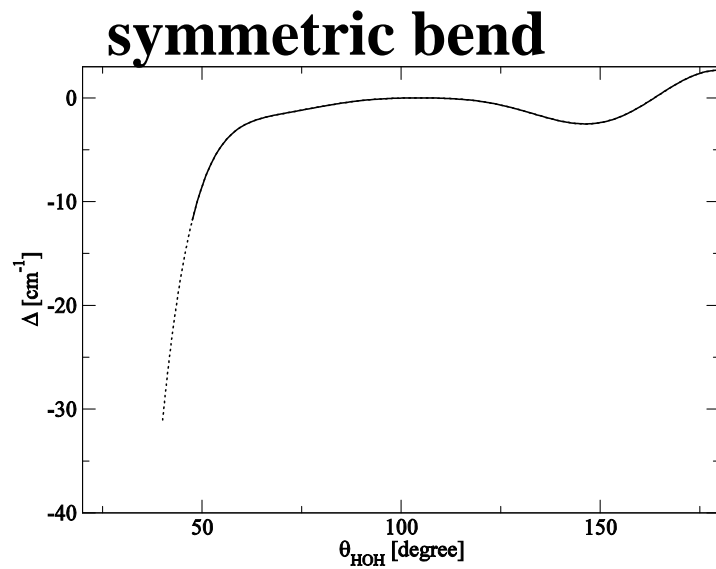
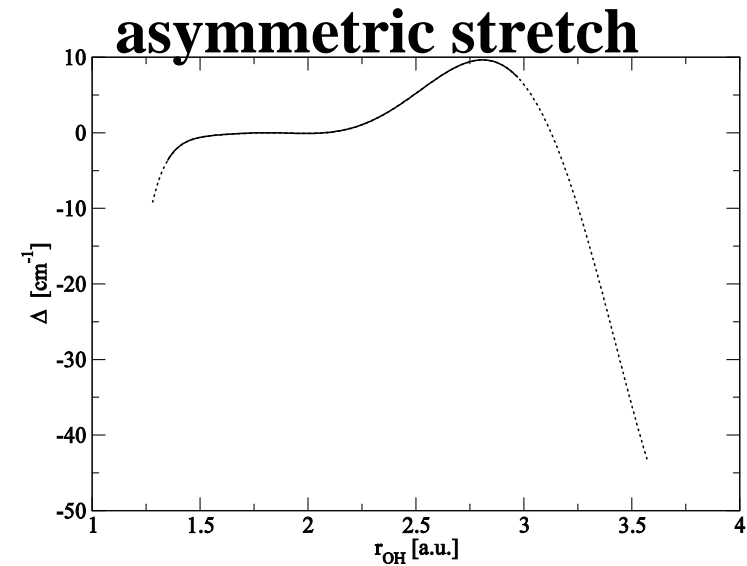
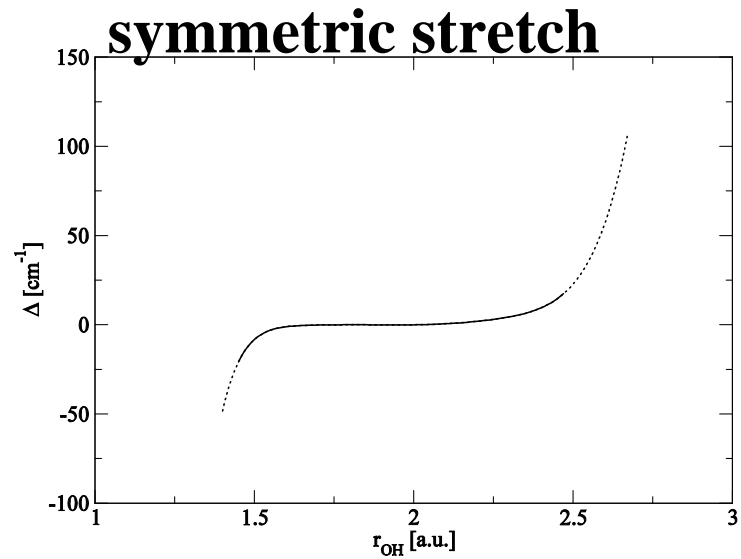
Gaunt and Breit corrections

quantum electrodynamics (QED)

Adiabatic and nonadiabatic Born-Oppenheimer corrections

O. L. Polyansky, A. G. Császár, J. Tennyson, P. Barletta, S. V. Shirin, N. F. Zobov, D. W. Schwenke, and P. J. Knowles, *Science* **299**, 539 (2003).

Ab initio (CVRQD) – empirical (FIS3)



Stationary points on PESs

Equilibrium and effective structures of water

	$r/\text{\AA}$	$\Theta/\text{degrees}$
Born-Oppenheimer	0.957 82	104.48 ₅
Adiabatic (H ₂ ¹⁶ O)	0.957 85	104.50 ₀
(D ₂ ¹⁶ O)	0.957 83	104.49 ₀
Spectroscopic	0.957 77	104.48
Effective (r_g) (H ₂ ¹⁶ O)	0.97625	103.96
(300 K) (D ₂ ¹⁶ O)	0.97136	104.03

A. G. Császár, G. Czakó, T. Furtenbacher, J. Tennyson, V. Szalay, S. V. Shirin, N. F. Zobov, O. L. Polyansky, *J. Chem. Phys.* **122**, 214305 (2005).

G. Czakó, E. Mátyus, A. G. Császár, *J. Phys. Chem. A* in print (2009).

$J = 1$ rotational term values for the ground vibrational state of water from the CVRQD *ab initio* PESs

	H_2^{16}O		H_2^{18}O	
	CVRQD	MARVEL	CVRQD	MARVEL
1_{01}	23.795	23.7944	23.756	23.7549
1_{11}	37.138	37.1371	36.749	36.7486
1_{10}	42.372	42.3717	42.024	42.0234
4_{22}	315.799	315.779		

Beyond the BO approximation

- Diagonal Born-Oppenheimer correction (DBOC)
⇒ **adiabatic (mass-dependent) PES**

$$E_{\text{DBOC}} = -\langle \Psi_e | \sum_{\alpha} \frac{\nabla_{\alpha}^2}{2M_{\alpha}} | \Psi_e \rangle =$$
$$- \sum_{\alpha} \frac{\nabla_{\alpha}^2}{2M_{\alpha}} \left[2 \sum_i^{\text{occ}} f_i \langle \phi_i | \nabla_{\alpha}^2 | \phi_i \rangle + \sum_{ij}^{\text{occ}} \beta_{ij} \langle \phi_i | \nabla_{\alpha} | \phi_j \rangle \cdot \langle \phi_j | \nabla_{\alpha} | \phi_i \rangle \right]$$

- Nonadiabatic correction

Complicated correction to the kinetic energy operator

Challenge #2: Dipole moment surfaces

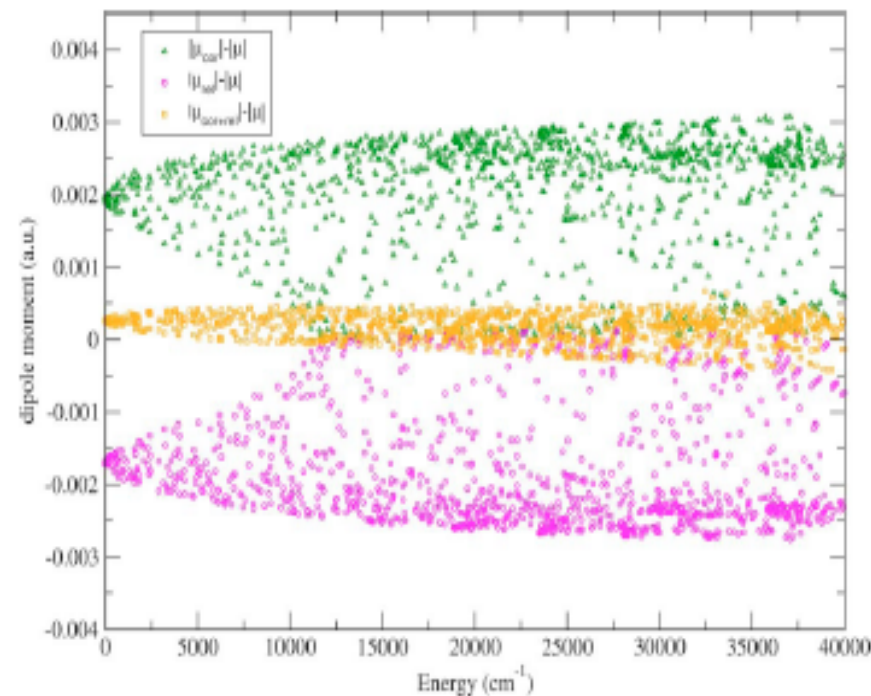
Compute strength of rovibrational lines as

$$S_{ij} = \left| \sum_k \langle i | \mu_k | j \rangle \right|^2$$

- Only rigorous selection rules remain
- All weak transitions are automatically included
- Most easily done in DVR (exceedingly simple property calculations)
- Relatively expensive for larger(r) calculation
- Potentially more accurate than most experiment

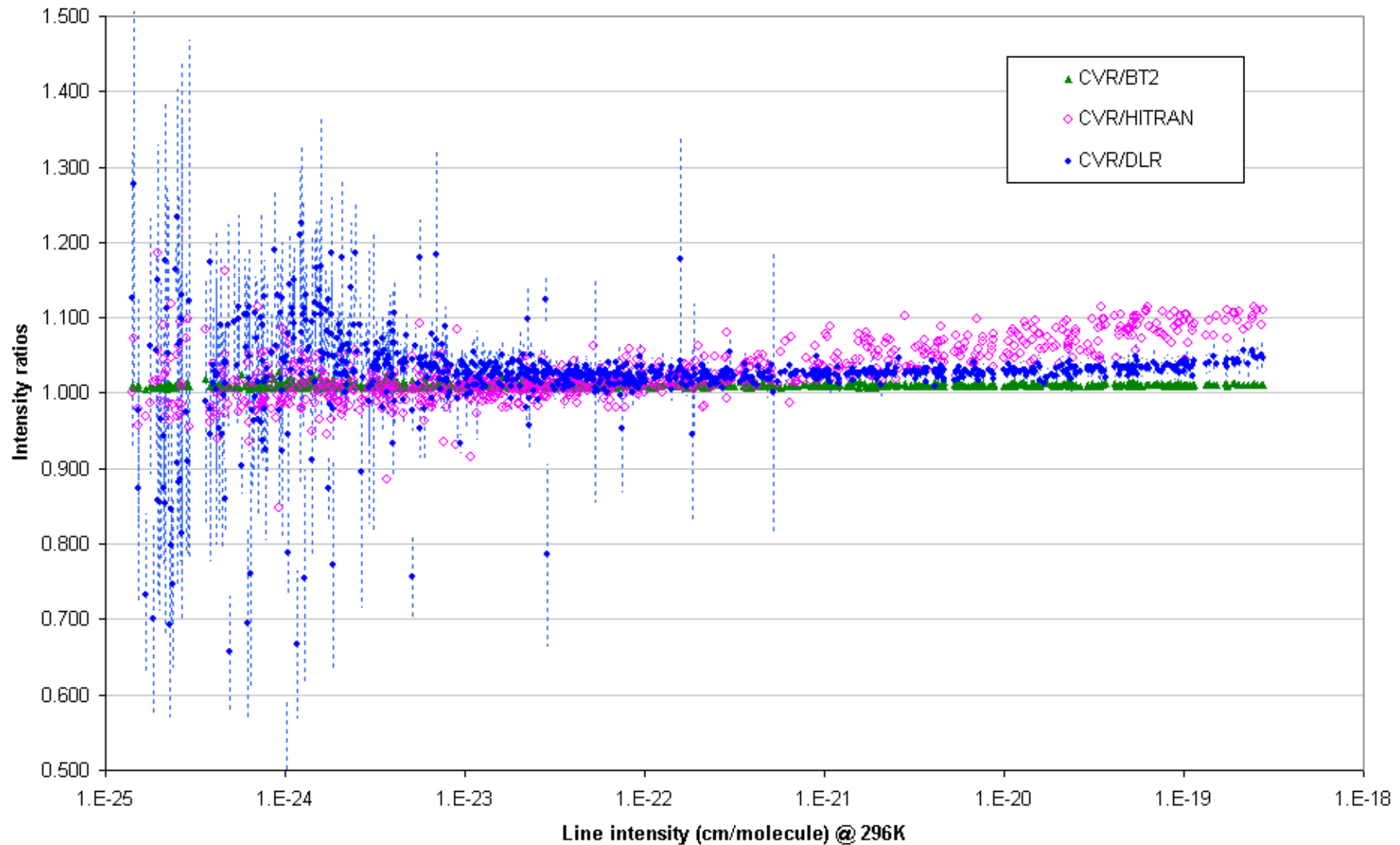
The CVR DMS of water

- Ground-state dipole moment of water:
 - best computed: 1.8539(13) D
 - best measured: 1.8546(6) D
- Relativistic and core corrections to the valence-only dipole surface cancel each other almost completely
- The computed DMS is not very sensitive to the choice of the Gaussian basis set



L. Lodi, R. N. Tolchenov, J. Tennyson, A. E. Lynas-Gray, S. V. Shirin, N. F. Zobov, O. L. Polyansky, A. G. Császár, J. N. P. van Stralen, and L. Visscher, *J. Chem. Phys.* **2008**, *128*, 044304.

Quality of the CVR DMS of water



L. Lodi, R. N. Tolchenov, J. Tennyson, A. E. Lynas-Gray, S. V. Shirin, N. F. Zobov, O. L. Polyansky, A. G. Császár, J. N. P. van Stralen, and L. Visscher, *J. Chem. Phys.* **2008**, *128*, 044304.

Challenge #3: Nuclear motion problem

- **Qualitative understanding of atomic motion**
RRHO (rigid rotor – harmonic oscillator)
 - SQM force fields, GF method, simple model problems
- **Interpretation of experimental results**
Perturbative approaches, anharmonic force fields
 - Local vs normal modes, VPT2, higher-order PT
- **Moving beyond experimental capabilities**
Variational approaches
 - VBR**Grid-based** (nearly variational) approaches
 - FBR DVR

Grid-based techniques in natural sciences

- **Discrete Ordinate Method** (DOM, atmospheric sciences for 3D radiative transfer, DOTS with time stepping)
- **Quadrature Discretization Method** (QDM, kinetic theory, Fokker-Planck equation)
- **Lagrange mesh** (LM, quantum mechanics)
- **Fourier grid Hamiltonian** (FGH, time-dependent quantum mechanics)
- **Discrete Variable Representation** (DVR, molecular spectroscopy) with (optimal) generalized (GDVR) variants

Standard DVR versus FBR

DVR advantages

- Diagonal in the potential (quadrature approximation)
 $\langle \alpha | V | \beta \rangle = \delta_{\alpha\beta} V(x_\alpha)$, no need for integration
- Analytic evaluation of kinetic energy matrix elements
- Optimal truncation and diagonalization based on adiabatic separation
- Sparse Hamiltonian matrix with product basis
- Easy property evaluations: i th element of the n th eigenvector proportional to the value of the n th eigenfunction at the i th quadrature point

DVR disadvantages

- Not strictly variational (quadrature and truncation error couple, difficult to do small calculations)
- Problems with coupled basis sets [back to optimal (G)FBR (and GDVR)]
- Inefficient for non-orthogonal coordinate systems

Transformation between DVR and FBR quick & simple for standard DVR

**I. Tailor-made approach: prederived,
analytic, case-dependent T ,
unique code for each molecule**

**The simplest grid-based procedure to solve
the triatomic rovibrational problem variationally:**

The DOPI algorithm

Discrete Variable Representation of the Hamiltonian

Energy operator in orthogonal (**O**) coordinate system

Direct product (**P**) basis

Diagonalization with an iterative (**I**) technique (*e.g.*, Lánczos)

G. Czakó, T. Furtenbacher, A. G. Császár, and V. Szalay, *Mol. Phys. (Nicholas C. Handy Special Issue)* **102**, 2411 (2004).

$$\hat{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \text{ctg} \theta \frac{\partial}{\partial \theta} \right) + \hat{V}(R_1, R_2, \cos \theta)$$

$$(\mathbf{R}_j^{-2})_{n_j, n'_j} = \frac{1}{2\mu_j q_{n_j}^2} \delta_{n_j, n'_j}$$

$$(\mathbf{K})_{\ell, \ell'} = \mathbf{T}^+ \begin{pmatrix} 0.1 & 0 & \cdot & 0 \\ 0 & 1.2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & 0 & (L-2)(L-1) \end{pmatrix} \mathbf{T}$$

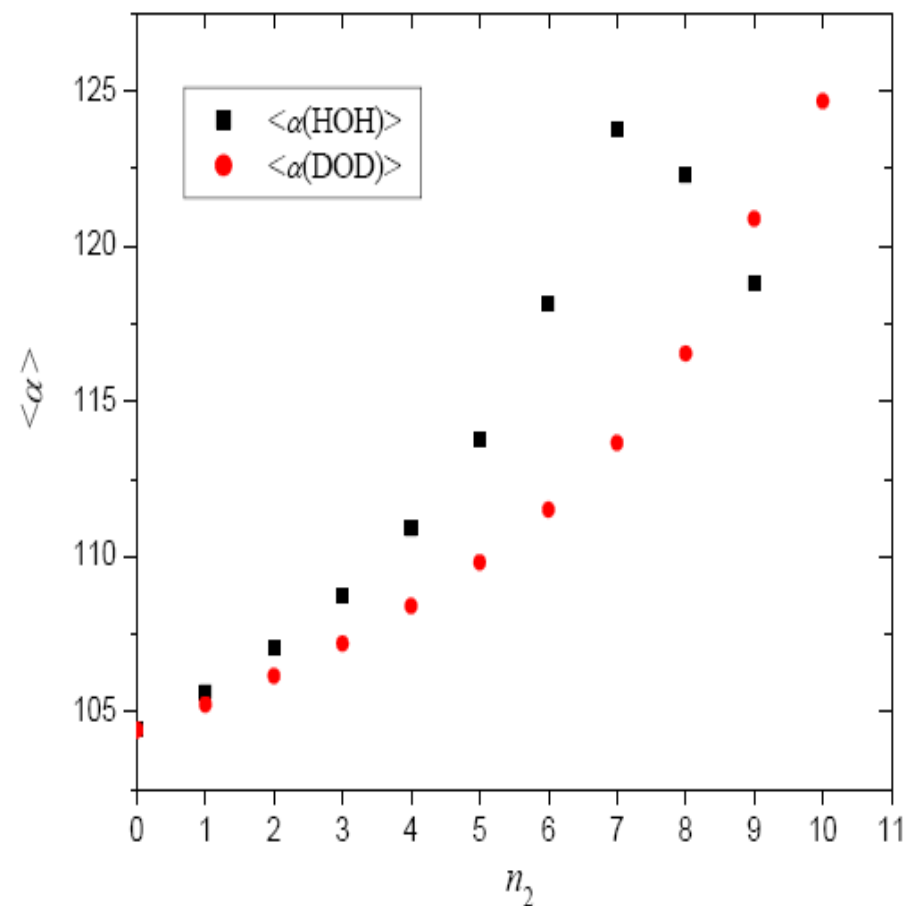
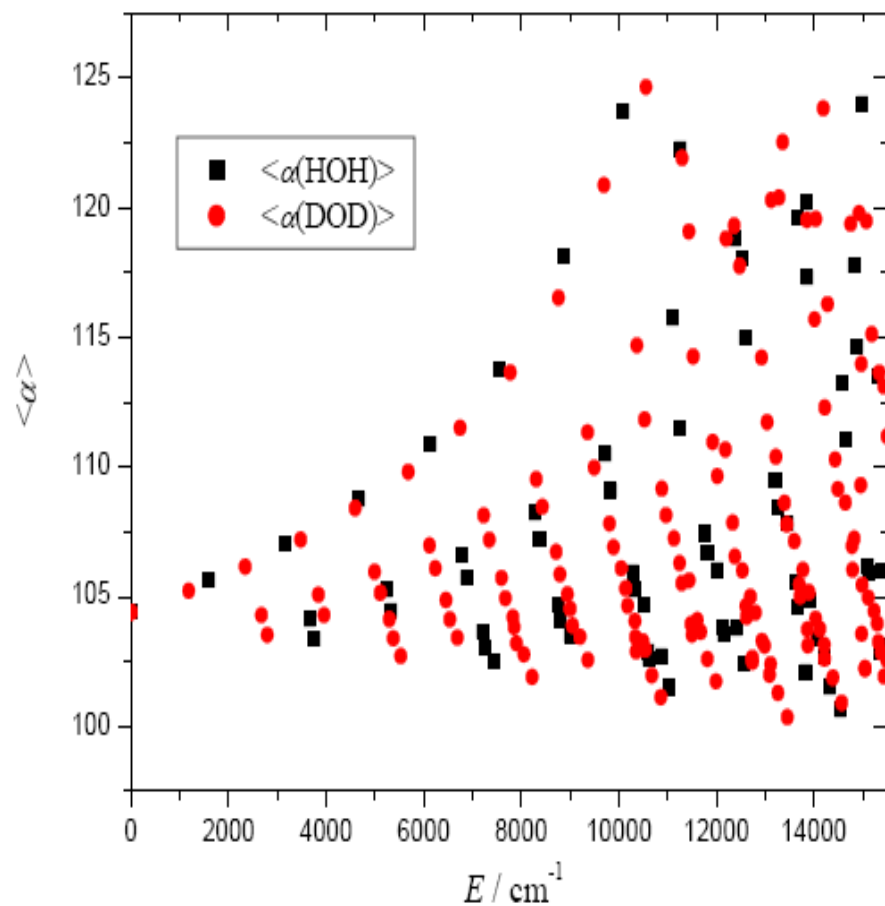
$$(\mathbf{K}_{R_j})_{n_j, n'_j} = \left\langle \chi_{n_j}(R_j) \left| -\frac{1}{2\mu_j} \frac{\partial^2}{\partial R_j^2} \right| \chi_{n'_j}(R_j) \right\rangle$$

$$(\mathbf{V}^{\text{diag}})_{n_1 n_2 \ell, n'_1 n'_2 \ell'} = V(q_{n_1}, q_{n_2}, q_\ell)_{n_1 n_2 \ell, n'_1 n'_2 \ell'}$$

$$\mathbf{H}^{\text{DVR}} = \mathbf{K}_{R_1} \otimes \mathbf{I}_{R_2} \otimes \mathbf{I} + \mathbf{I}_{R_1} \otimes \mathbf{K}_{R_2} \otimes \mathbf{I} + \mathbf{R}_1^{-2} \otimes \mathbf{I}_{R_2} \otimes \mathbf{K} + \mathbf{I}_{R_1} \otimes \mathbf{R}_2^{-2} \otimes \mathbf{K} + \mathbf{V}^{\text{diag}}$$

Sparse matrix \longrightarrow Special iterative Lánczos „diagonalization”

Variationally computed expectation values of the bond angles of H_2^{16}O and D_2^{16}O



II. Generic Hamiltonian: DEWE

(Discrete Variable Representation – Eckart-Watson Hamiltonian – Exact inclusion of the potential energy)

1. Eckart-Watson vibrational operator (normal coordinates: Eckart-system, orthogonal, rectilinear internal coordinates):

$$\hat{H} = \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - \frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}^2 + V$$

2. Numerically exact inclusion of arbitrary (e.g., valence) coordinate potential energy surface

$$\mathbf{r}_{pi} = \mathbf{C} \left[\mathbf{c}_i - \mathbf{c}_p + \sum_{k=1}^{3N-6} \left(\frac{1}{\sqrt{m_i}} \mathbf{l}_{ik} - \frac{1}{\sqrt{m_p}} \mathbf{l}_{pk} \right) Q_k \right]$$

3. Matrix of Hamiltonian in DVR representation, on-the-fly (impossible to store even the nonzero elements of the sparse Hamiltonian) iterative eigenvalue and eigenvector computation (Lánczos).

E. Mátyus, G. Czakó, B. T. Sutcliffe, A. G. Császár, *J. Chem. Phys.* **127**, 084102 (2007).

E. Mátyus, J. Šimunek, A. G. Császár, *J. Chem. Phys.* **131**, 074106 (2009).

DEWE

(Discrete Variable Representation – Eckart-Watson Hamiltonian – Exact inclusion of the potential energy)

3. a) Direct-product basis ($N = n^D, D = 3N-6$). For example, $D = 3$

$$\begin{array}{ccc} \sim O(N^{1+\frac{1}{D}}) & \mathbf{H} & \sim O(N^{1+\frac{2}{D}}) \\ \begin{array}{c} \text{[Diagram of sparse matrix structure with diagonal and off-diagonal blocks]} \end{array} & & \begin{array}{c} \text{[Diagram of dense matrix structure with a central block]} \end{array} \end{array}$$

3. b) In iterative „diagonalization” algorithms explicit knowledge of \mathbf{H} is not needed, enough to form $\mathbf{y}^{\text{Lanczos}} = \mathbf{H}\mathbf{x}^{\text{in}}$:

$$\mathbf{y}^{\text{Lanczos}} = \left(\sum_{\alpha\beta} \alpha \boldsymbol{\mu}_{\alpha\beta} \beta \right) \mathbf{x}^{\text{in}} = \sum_{\alpha\beta} \left(\alpha \left(\boldsymbol{\mu}_{\alpha\beta} \left(\beta \mathbf{x}^{\text{in}} \right) \right) \right)$$

On-the-fly computation of Hamilton-matrix – Lánczos vector multiplication.

E. Mátyus, G. Czakó, B. T. Sutcliffe, A. G. Császár, *J. Chem. Phys.* **127**, 084102 (2007).

E. Mátyus, J. Šimunek, A. G. Császár, *J. Chem. Phys.* **131**, 074106 (2009).

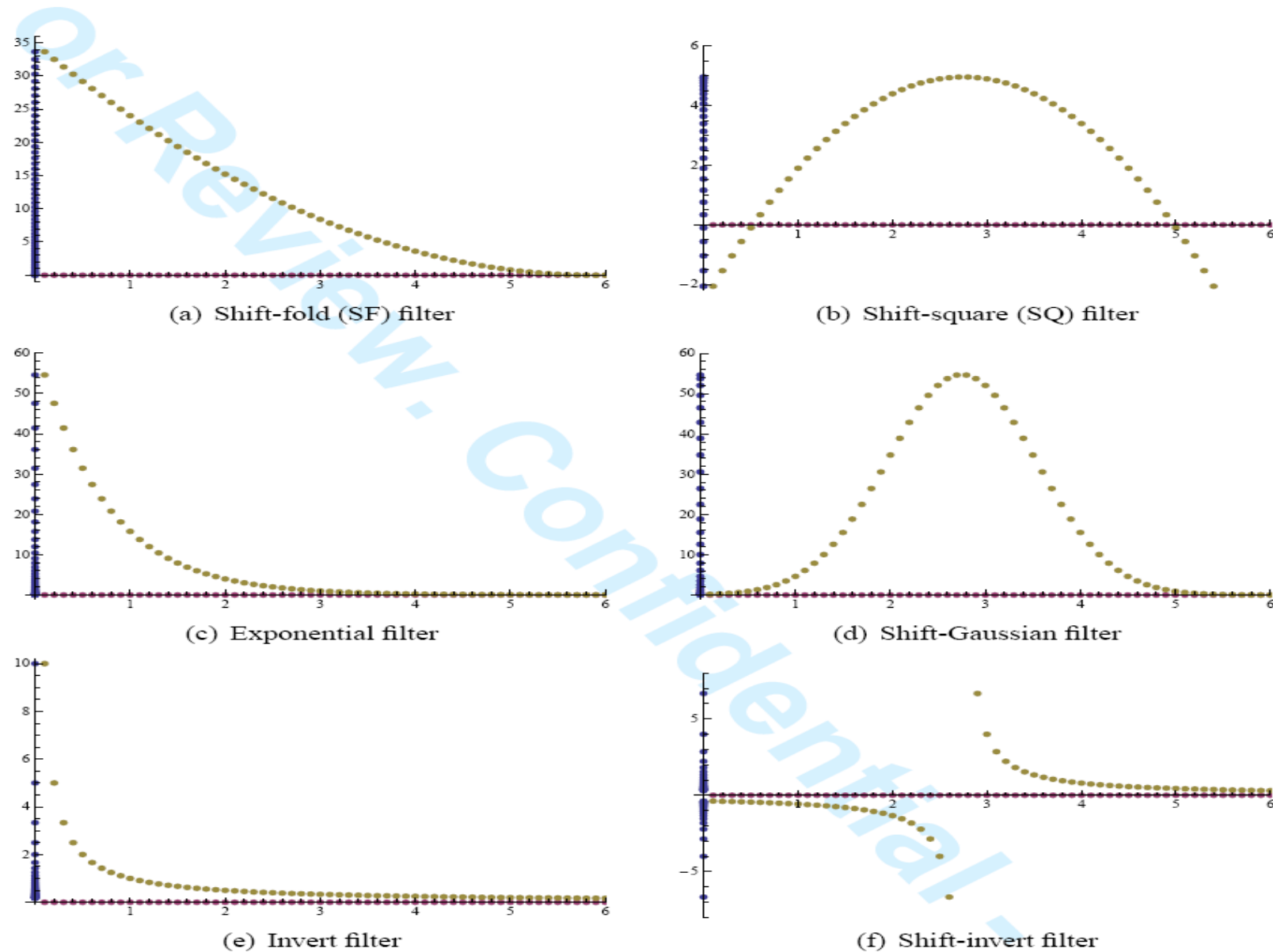


Figure 2: Schematic representation of different spectral transformation techniques. Line positions of the original and transformed spectrum are represented on the x - and y -axes (red and blue circles), respectively. The graphs of the transformation functions are also plotted at discrete points (brown circles) on the $x - y$ plane. See the mathematical definition of the filters presented on plots (a)–(f) in the text.

Vibrational transitions of $^{12}\text{CH}_4$ (cm^{-1})

$$\hat{W}_{nm} = n \cdot \frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - m \cdot \frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}_k^2 + V, \quad n, m = 0, 1$$

$(n_1 n_3)(n_2 n_4)\text{sym}$	$\hat{W}_{00}^{\text{a,b}}$	$\hat{W}_{01}^{\text{a,b}}$	$\hat{W}_{10}^{\text{a,b}}$	$\hat{W}_{11}^{\text{a,c}}$	Ref. 43
(00)(00)A1	9690.9 (0.6)	9686.9 (4.6)	9695.4 (-3.9)	9691.5 (0.0)	9691.5
(00)(01)F2	1299.9 (11.6)	1299.9 (11.6)	1311.6 (-0.1)	1311.5 (0.2)	1311.7
	1300.0 (11.7)	1300.0 (11.7)	1311.7 (0.0)	1311.7 (0.0)	1311.7
	1300.1 (11.6)	1300.1 (11.6)	1311.7 (0.0)	1311.7 (0.0)	1311.7
(00)(10)E	1524.2 (9.0)	1524.2 (9.0)	1533.2 (0.0)	1533.2 (0.1)	1533.3
	1524.2 (9.1)	1524.2 (9.1)	1533.3 (0.0)	1533.3 (0.0)	1533.3

Normal Mode Distribution (NMD)

$$NMD_{ij}^2 = \langle \psi_i | Q_J^{\text{HO}} \rangle^2$$

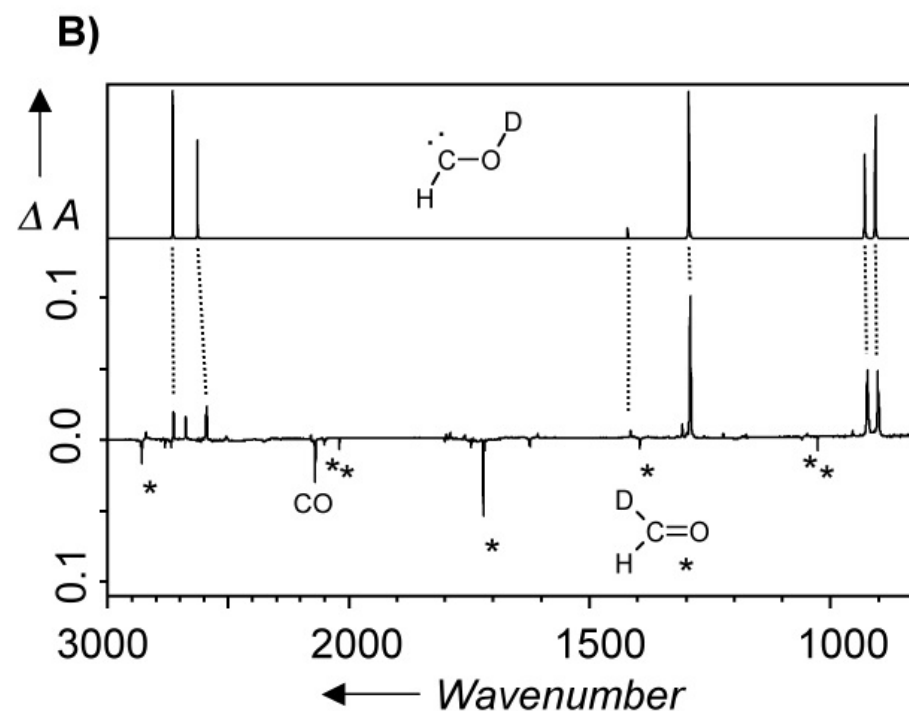
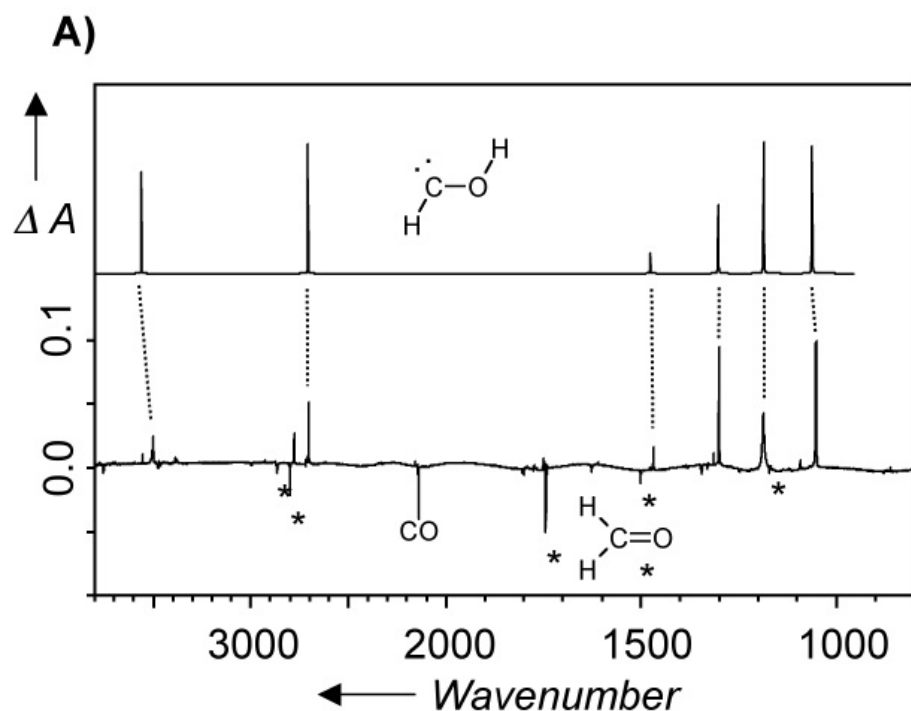
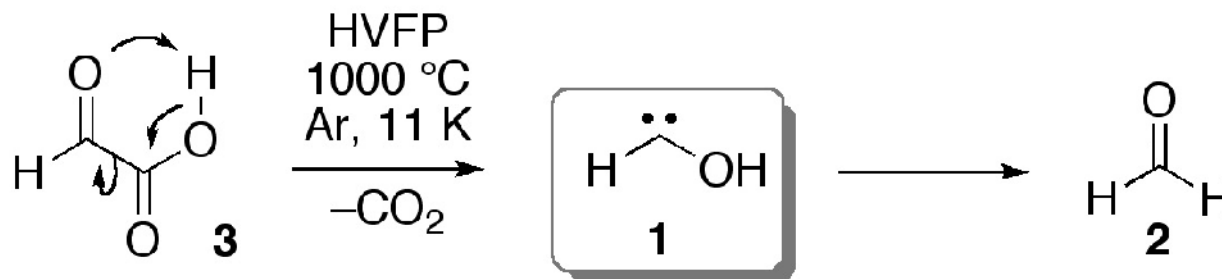
HNCO

„Fundamentals”

	4681.3	572.4	637.0	818.1	1144.8	1209.4	1274.0	1318.3	1390.5	1455.1	1636.2	1717.2	1781.8	Sum	
	Q_0	Q_5	Q_6	Q_4	Q_{5+5}	Q_{5+6}	Q_{6+6}	Q_3	Q_{4+5}	Q_{4+6}	Q_{4+4}	Q_{5+5+5}	Q_{5+5+6}		
4631.0	98	0	0	0	0	0	0	0	0	0	0	0	0	...	99
579.5	0	95	0	1	0	0	0	0	0	0	0	0	0	...	97
660.2	0	0	99	0	0	0	0	0	0	0	0	0	0	...	99
780.7	0	2	0	90	0	0	0	0	0	0	2	0	0	...	96
1146.8	0	0	0	0	80	0	6	5	0	0	0	0	0	...	93
1267.1	0	0	0	0	3	0	26	41	20	0	0	0	0	...	94
1275.1	0	0	0	0	0	91	0	0	0	5	0	0	0	...	97
1329.3	0	0	0	2	4	0	11	45	22	0	4	0	0	...	92
1358.6	0	0	0	2	7	0	54	5	15	0	7	0	0	...	93
1476.6	0	0	0	0	0	7	0	0	0	88	0	0	0	...	97
1521.6	0	0	0	2	0	0	2	0	28	0	51	0	0	...	91
1712.7	0	0	0	0	0	0	0	0	0	0	0	69	0	...	90
1843.6	0	0	0	0	0	0	0	0	0	0	0	0	45	...	96
...	
Sum	98	99	98	95	98	99	99	94	98	95	92	95	98		

L. Woodcock, W. D. Allen, H. F. Schaefer III, I. Kozin, E. Mátyus, G. Czakó, A. G. Császár,
J. Phys. Chem. A **2008**, to be submitted.

Detection of elusive HCOH through matrix isolation i.r. spectroscopy



P. R. Schreiner, H. P. Reisenauer, F. Pickard, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **453**, 906 (2008).

III. GENIUSH: General ro vib code with Numerical, Internal-Coordinate, User-Specified Hamiltonians

(general code – full- of reduced-dimensional rovibrational problem – internal coordinate Hamiltonian with numerical computation of both T and V – discrete variable representation)

Initial specifications

- body-fixed frame (*e.g.*, Eckart, principal axis, „xxy” gauge)
- set of internal coordinates (*e.g.*, Z-matrix, Radau)
- constraints for the coordinates if necessary
- Cartesian coordinates of the atoms

„Main” program

- numerical or analytical 1st, 2nd, and 3rd derivatives of Euler angles and internal coordinates in terms of Cartesians and vice versa
- numerically compute \mathbf{G} matrix, U , and V at every grid point
- determine needed eigenpairs via variants of Lánczos’ algorithm

Result: single code for all full- or reduced-dimensionality problems for molecules with arbitrary number of „interacting” minima

E. Mátyus, G. Czakó, A. G. Császár, *J. Chem. Phys.* **130**, 134112 (2009).

Vibrational Hamiltonians

$$\hat{H}^{\text{Cartesian}} = -\frac{\hbar^2}{2} \sum_{i=1}^N \frac{1}{m_i} \nabla_i^2 + V$$

$$\hat{H}^{\text{Podolsky}} = \frac{1}{2} \sum_{kl=1}^D \tilde{g}^{-1/4} \hat{p}_k G_{kl} \tilde{g}^{1/2} \hat{p}_l \tilde{g}^{-1/4} + V \quad D \leq 3N - 6$$

$$\hat{H}^{\text{rearranged}} = \frac{1}{2} \sum_{kl=1}^D \hat{p}_k G_{kl} \hat{p}_l + U + V \quad D \leq 3N - 6$$

$$\text{with } U = \frac{\hbar^2}{32} \sum_{kl=1}^D \left[\frac{G_{kl}}{\tilde{g}^2} \frac{\partial \tilde{g}}{\partial q_k} \frac{\partial \tilde{g}}{\partial q_l} + 4 \frac{\partial}{\partial q_k} \left(\frac{G_{kl}}{\tilde{g}} \frac{\partial \tilde{g}}{\partial q_l} \right) \right]$$

Some numerical considerations

t-vector vs. **s**-vector formalism

the former seems to be better

$$\partial^n \mathbf{x}_i / \partial q_k^n$$

$n = 1$ for Podolsky form

$n = 1, 2, 3$ for rearranged form

fast, on-the-fly Hamiltonian multiplication

$$\mathbf{y} = \mathbf{H}^{\text{VP}} \mathbf{x}^{\text{in}} = \frac{1}{2} \tilde{\mathbf{g}}^{-1/4} \sum_{k=1}^D \left(\mathbf{p}_k \sum_{l=1}^D \left(\mathbf{G}_{kl} \tilde{\mathbf{g}}^{1/2} \left(\mathbf{p}_l \tilde{\mathbf{g}}^{-1/4} \mathbf{x}^{\text{in}} \right) \right) \right) + \mathbf{V} \mathbf{x}^{\text{in}}$$

Full-dimensional (3D) and „local-mode” (2D) water

Label	Full-dim.	Local-mode
$(1\ 0\ 0) = (1\ 0)^{+0}$	3657.05	3666.93
$(0\ 0\ 1) = (1\ 0)^{-0}$	3755.73	3777.22
$(2\ 0\ 0) = (2\ 0)^{+0}$	7201.19	7224.87
$(1\ 0\ 1) = (2\ 0)^{-0}$	7249.22	7283.78
$(0\ 0\ 2) = (1\ 0)^{+0}$	7444.88	7494.73
$(5\ 0\ 0) = (5\ 0)^{+0}$	16898.27	16994.58
$(4\ 0\ 1) = (5\ 0)^{-0}$	16898.84	16993.96
$(4\ 0\ 2) = (5\ 1)^{+0}$	20533.50	20655.92
$(3\ 0\ 3) = (5\ 1)^{-0}$	20543.14	20673.74

A system with two „interacting” minima: NH₃

Table 2: Internal coordinates of NH₃: $r_1, r_2, r_3, \theta, \beta_1, \beta_2$.

N						
X	N	1.0				
H1	N	r_1	X	θ		
H2	N	r_2	X	θ	H1	β_1
H3	N	r_3	X	θ	H1	β_2

GENIUSH	Reference	GENIUSH	Reference
7436.82 (A ₁ ')	n.a.	1597.26 (A ₁ ')	1597.38
0.79 (A ₂ '')	0.79	1625. 62 (E ₁ ')	1626.22
932.41 (A ₁ ')	932.46	1626.73 (E ₁ '')	1627.33
968.15 (A ₂ '')	968.14	1882.18 (A ₂ '')	1882.09

Summary 1.

The MARVEL algorithm allows the determination of exceedingly accurate „empirical” rovibrational energy levels and thus should help the assignment of spectra of molecules of arbitrary size and with arbitrary number of observed transitions in any region of the EM spectrum.

The composite focal-point analysis (FPA) approach is the most suitable way to generate highly accurate PESs and DMSs. (Note that it has been widely used for much less demanding thermochemical applications.)

We now have exceedingly accurate PESs (CVRQD) and DMSs (CVR) for the main isotopologues of water, helping finally to understand the spectroscopy of water vapor and thus the major part of the greenhouse effect on Earth.

Summary 2.

The DOPI procedure, using a tailor-made kinetic energy operator, is our favored technique for the solution of the triatomic variational rovibrational problem when the goal is to match experiments (H_3^+ and H_2O), compute full rovibrational spectra (IUPAC TG), and estimate rovibrational averages.

The DEWE protocol, through numerically exact inclusion of arbitrary PESs together with the Eckart-Watson Hamiltonian, allows the efficient determination and characterization (NMD, rotational overlaps) of spectra of molecules having a single well-defined potential well (*e.g.*, methane).

The GENIUSH technique, using fully numerical operators based on user specifications, offers a general approach to spectroscopic and dynamical problems (thus mimicking electronic structure computations) but much more work needs to be done so that it can compute linelists.

Challenges left for the (near?) future

- (1) Determination of a full (truly global) accurate PES for many-electron systems (no refinement of the PES is needed)
- (2) Doing nuclear motion calculations close to the dissociation asymptotes
- (3) Handling of nonadiabaticity and cases with several surfaces
- (4) Getting away from fitting of PESs
- (5) Treatment(s) without the Born-Oppenheimer approximation
- (6) Effective extension of the nuclear motion calculation to many more dimensions (atoms)
- (7) Use of the efficient nuclear motion techniques developed in related fields, like reaction kinetics (CRP), reaction dynamics, and optimal quantum control
- (8) Spectropedia