

LECTURE #2

TRIATOMIC MOLECULES:

TAILOR-MADE APPROACHES

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Winter School in Theoretical Chemistry
Helsinki, Finland, December 17-20, 2012



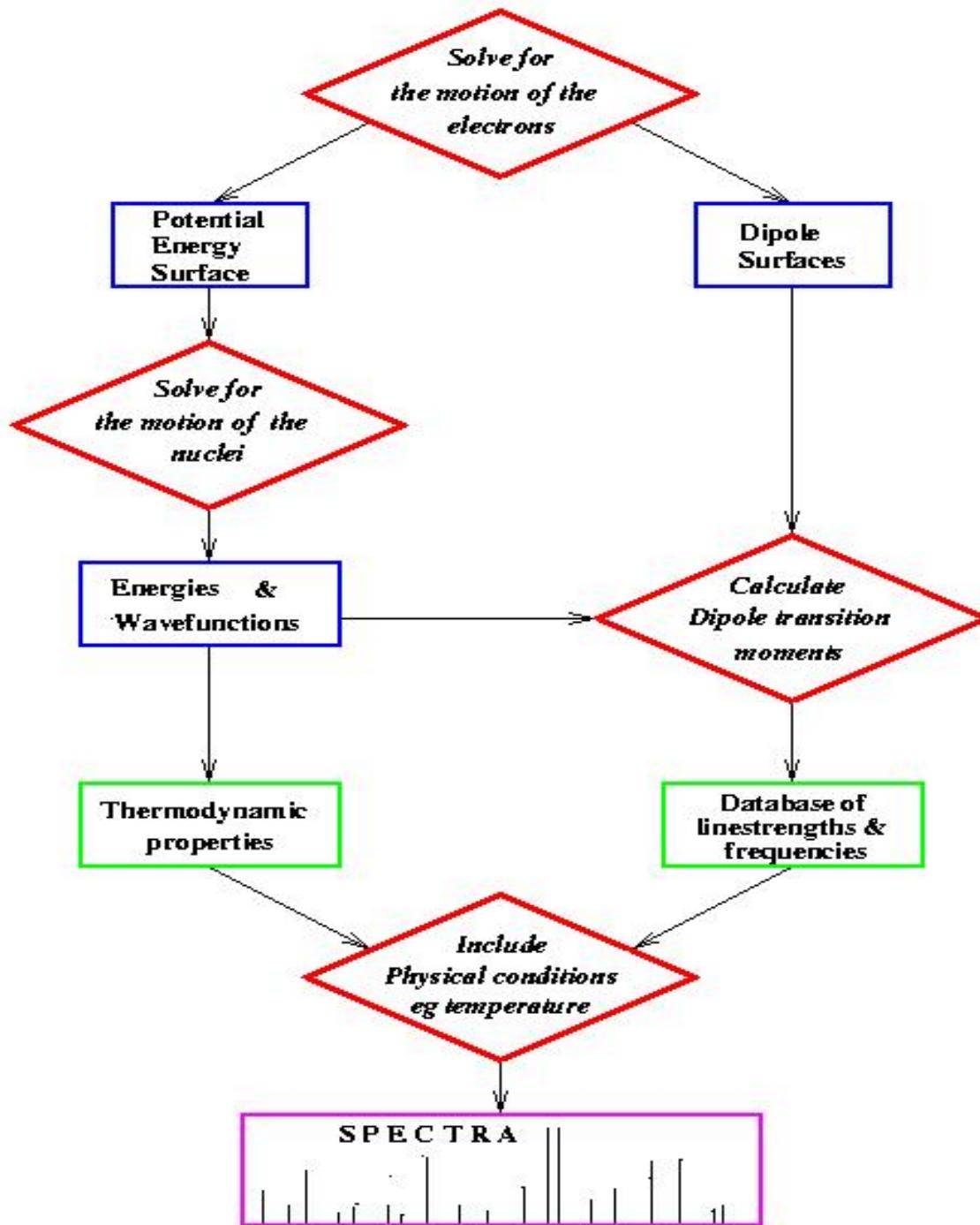
OUTLINE

- **Introduction**
- **The D³OPI and D²FOPI approaches**
- **Spectroscopic and structural applications and implications**
- **Summary and outlook**

The variational approach

Provides a complete theoretical treatment
with no/minimal *a priori* assumptions
and no/minimal *a posteriori* corrections

- Treats molecular vibrations and rotations at the same time (6-D problem for triatomics)
- Interprets experimental results in terms of potential energy surface(s), PES, and dipole moment surface (DMS)
- Only assumes rigorous quantum numbers:
 J , p , symmetry (e.g., ortho/para)
- Results in spectra if DMS is available
- Works irrespective of perturbations of energy levels



Source: J. Tennyson

Choices to be made during the design of a variational nuclear motion algorithm

- coordinates (**vibrational** and **rotational**)
- derivation of the analytic form of the **kinetic energy operator** corresponding to the chosen set of coordinates and the chosen **embedding**
- determination of potential energy surface (**PES**)
- selection of **basis** functions
- computation of **matrix elements** of the Hamiltonian
- “**diagonalization**” of the Hamiltonian

(Lecturer: Janne Pesonen)

**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 D³OPI and D²FOPI algorithms

Discrete Variable Representation of the Hamiltonian

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

Direct-product (**P**) basis

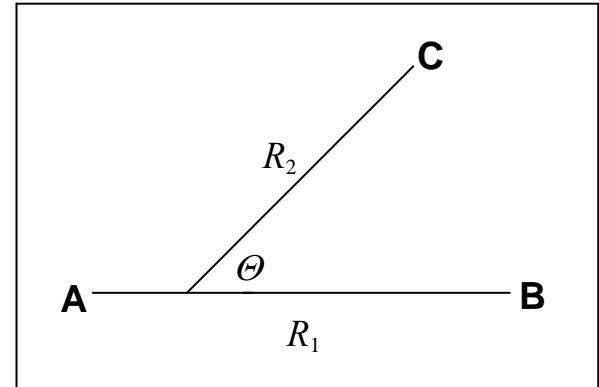
Diagonalization with an iterative (**I**) technique (e.g., Lánczos)

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

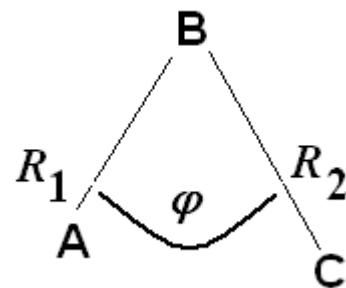
T. Szidarovszky, A. G. Császár, and G. Czakó, *PCCP* **12**, 8373 (2010).

Coordinates

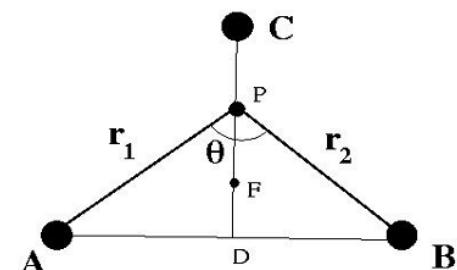
Jacobi (scattering) coordinates
(1842)



simple internal coordinates



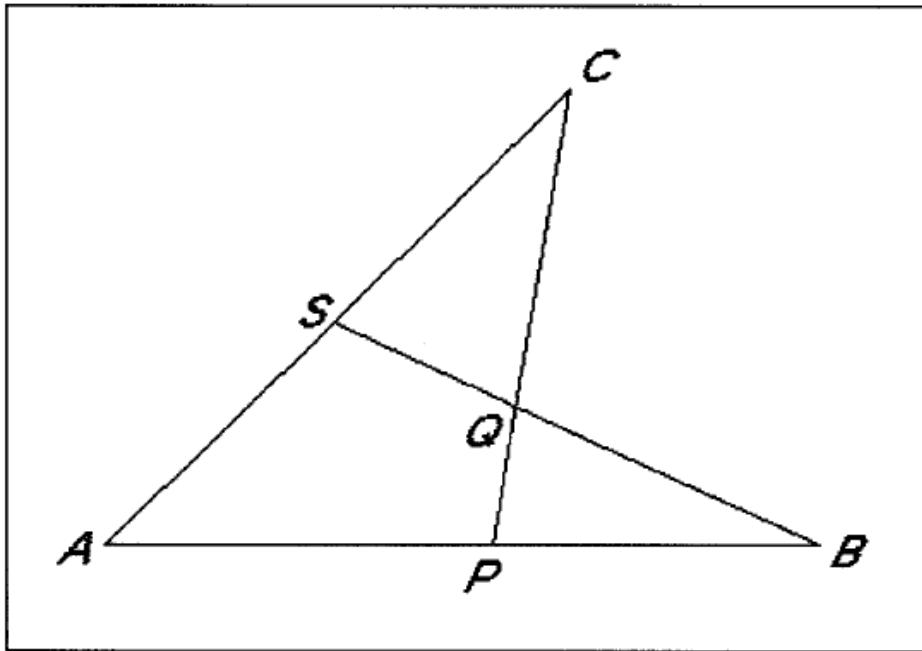
Radau coordinates
(1868)



Radau coordinates: $F = ABC$ centre of mass
 $PD \times PD = CD \times FD$

Coordinates (Sutcliffe and Tennyson)

$$g_1 = \frac{A - P}{A - B}$$



$$g_2 = \frac{A - S}{A - C}$$

$$R_1 = B - S \quad R_2 = C - P \quad \Theta = BQC$$

Jacobi coordinates: internal coordinates: Radau coordinates:

$$g_1 = \frac{m_B}{m_A + m_B} \quad g_2 = 0$$

$$g_1 = g_2 = 0$$

$$g_1 = 1 - \frac{\alpha}{\alpha + \beta - \alpha\beta}$$

$$g_2 = 1 - \frac{\alpha}{1 - \beta + \alpha\beta}$$

Vibrational kinetic energy operator

$$\hat{K} = \hat{K}_1 + \hat{K}_2$$

$$\hat{K}_1 = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \left(\frac{\hbar^2}{2\mu_1 R_1^2} + \frac{\hbar^2}{2\mu_2 R_2^2} \right) \left(\frac{\partial^2}{\partial \Theta^2} + \operatorname{ctg} \Theta \frac{\partial}{\partial \Theta} \right)$$

$$\hat{K}_2 = \frac{\hbar^2}{\mu_{12}} \left[-\cos \Theta \frac{\partial^2}{\partial R_1 \partial R_2} + \frac{\cos \Theta}{R_1 R_2} \left(\frac{\partial^2}{\partial \Theta^2} + \operatorname{ctg} \Theta \frac{\partial}{\partial \Theta} \right) + \sin \Theta \left(\frac{1}{R_1} \frac{\partial^2}{\partial R_2 \partial \Theta} + \frac{1}{R_2} \frac{\partial^2}{\partial R_1 \partial \Theta} + \frac{1}{R_1 R_2} \frac{\partial}{\partial \Theta} \right) \right]$$

$$\frac{1}{\mu_1} = \frac{g_2^2}{m_C} + \frac{1}{m_B} + \frac{(1-g_2)^2}{m_A}$$

$$\frac{1}{\mu_2} = \frac{1}{m_C} + \frac{g_1^2}{m_B} + \frac{(1-g_1)^2}{m_A}$$

$$\frac{1}{\mu_{12}} = -\frac{g_2}{m_C} - \frac{g_1}{m_B} + \frac{(1-g_1)(1-g_2)}{m_A}$$

$$dV = \sin \Theta dR_1 dR_2 d\Theta \quad (\text{volume element})$$

Rovibrational kinetic energy operator in orthogonal coordinates

$$\hat{H} = -\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2} \right) \left(\frac{\partial^2}{\partial \Theta^2} + \operatorname{ctg}(\Theta) \frac{\partial}{\partial \Theta} - \frac{\hat{j}_z^2}{\sin^2 \Theta} \right) + \frac{1}{2\mu_1 R_1^2} (J^2 - 2J_z j_z - J_+ j_- - J_- j_+) + \hat{V}(R_1, R_2, \Theta)$$

$$dV = \sin \Theta \sin \xi \, dR_1 dR_2 d\Theta d\varphi d\chi d\xi$$

The Sutcliffe-Tennyson Hamiltonian

$$\hat{H} = \hat{K}_V^{(1)} + \hat{K}_V^{(2)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + V(r_1, r_2, \theta)$$

where

$$\hat{K}_V^{(1)} = \delta_{jj'}\delta_{kk'} \left[-\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial r_2^2} + \frac{\hbar^2}{2} j(j+1) \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right) \right]$$

$$\begin{aligned} \hat{K}_V^{(2)} = & -\frac{\hbar^2}{\mu_{12}} \delta_{j'j+1} \delta_{kk'} d_{jk} \left(\frac{\partial}{\partial r_1} - \frac{j+1}{r_1} \right) \left(\frac{\partial}{\partial r_2} - \frac{j+1}{r_2} \right) \\ & - \frac{\hbar^2}{\mu_{12}} \delta_{j'j-1} \delta_{kk'} d_{j-1k} \left(\frac{\partial}{\partial r_1} + \frac{j}{r_1} \right) \left(\frac{\partial}{\partial r_2} + \frac{j}{r_2} \right) \end{aligned}$$

$$\hat{K}_{VR}^{(1)} = \delta_{jj'}\delta_{kk'} \frac{\hbar^2}{2\mu_1 r_1^2} (J(J+1) - 2k^2) - \delta_{jj'}\delta_{k'k\pm 1} \frac{\hbar^2}{2\mu_1 r_1^2} C_{jk}^\pm C_{jk}^\pm$$

$$\begin{aligned} \hat{K}_{VR}^{(2)} = & \delta_{j'j+1} \delta_{k'k+1} \frac{\hbar^2}{2\mu_{12}} C_{jk}^\pm \frac{a_{j\pm k}}{r_1} \left(\frac{j+1}{r_2} - \frac{\partial}{\partial r_2} \right) \\ & + \delta_{j'j-1} \delta_{k'k-1} \frac{\hbar^2}{2\mu_{12}} C_{jk}^\pm \frac{b_{j\pm k}}{r_1} \left(\frac{j}{r_2} + \frac{\partial}{\partial r_2} \right) \end{aligned}$$

Angular functions: $\Theta_{jk} D_{Mk}^J(\alpha, \beta, \gamma)$

Angular factors: $a_{jk}, b_{jk}, C_{jk}^\pm, d_{jk}$

$$\frac{1}{\mu_1} = \frac{g_2^2}{m_1} + \frac{1}{m_2} + \frac{(1-g_2)^2}{m_3}$$

$$\frac{1}{\mu_2} = \frac{1}{m_1} + \frac{g_1^2}{m_2} + \frac{(1-g_1)^2}{m_3}$$

$$\begin{aligned} \frac{1}{\mu_{12}} &= \frac{(1-g_1)(1-g_2)}{m_3} - \frac{g_2}{m_1} - \frac{g_1}{m_2} \\ &= 0 \text{ for orthogonal coordinates} \end{aligned}$$

Effective Hamiltonian after integration over angular and rotational coordinates.
Case where z is along r_1

Vibrational KE

Vibrational KE

Non-orthogonal coordinates only

Rotational & Coriolis terms

Rotational & Coriolis terms

Non-orthogonal coordinates only

Reduced masses

(g_1, g_2) defined by coordinates

Source: J. Tennyson

Challenge

How would the kinetic energy operator look like if the rotational and vibrational masses were different?

Non-adiabatic effects in the ST Hamiltonian

$$\hat{H} = \hat{K}_V^{\text{eff}} + \hat{K}_{VR}^{\text{eff}} + V^{\text{eff}}$$

where

$$\hat{K}_V = \hat{K}_V^{\text{eff}} - \delta_{kk'} \frac{k^2}{2 \sin^2 \theta} \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right)$$

$$\hat{K}_{VR} = \hat{K}_{VR}^{\text{eff}} + \delta_{kk'} \frac{k^2}{2 \sin^2 \theta} \left(\frac{1}{\mu_1 r_1^2} + \frac{1}{\mu_2 r_2^2} \right)$$

if $\mu^{\text{vib}} = \mu^{\text{rot}}$

$$\hat{K}_V + \hat{K}_{VR} = \hat{K}_V^{\text{eff}} + \hat{K}_{VR}^{\text{eff}}$$

if $\mu^{\text{vib}} \neq \mu^{\text{rot}}$

$$\hat{K}_V + \hat{K}_{VR} = \hat{K}_V^{\text{eff}} + \hat{K}_{VR}^{\text{eff}} + \hat{K}_{NBO}$$

$$\hat{K}_{NBO} = \delta_{kk'} \frac{k^2}{2 \sin^2 \theta} \left(\frac{s_1}{\mu_1 r_1^2} + \frac{s_2}{\mu_2 r_2^2} \right)$$

$$s_i = \frac{\mu_i^{\text{vib}}}{\mu_i^{\text{rot}}} - 1$$

$$V^{\text{eff}}(\underline{R}) = V_{\text{BO}}(\underline{R}) + V_{\text{rel}}(\underline{R}) + \frac{1}{\mu_S} \Delta V_{\text{sym}}^{\text{ad}}(\underline{R}) + \frac{1}{\mu_A} \Delta V_{\text{asym}}^{\text{ad}}(\underline{R})$$

Source: J. Tennyson

Open challenge

How would the kinetic energy operator look like if the rotational and vibrational masses would depend on the coordinates?

Basis functions

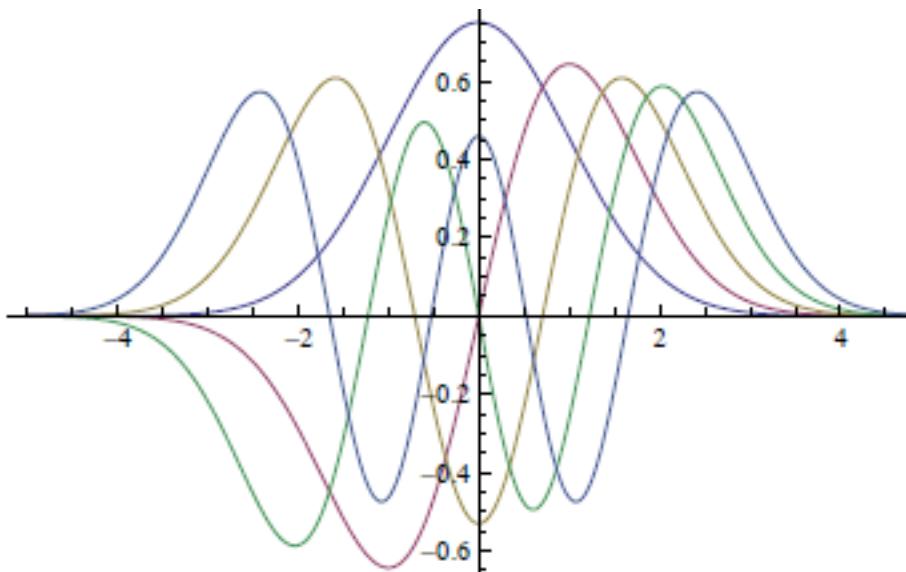
Vibrations

- one-dimensional orthogonal polynomial basis functions
 - Hermite-functions
 - Laguerre-functions and variants
 - Legendre-functions
 - Sinc basis, etc.
- multidimensional basis functions (one possible but not the preferred way to treat singularities)

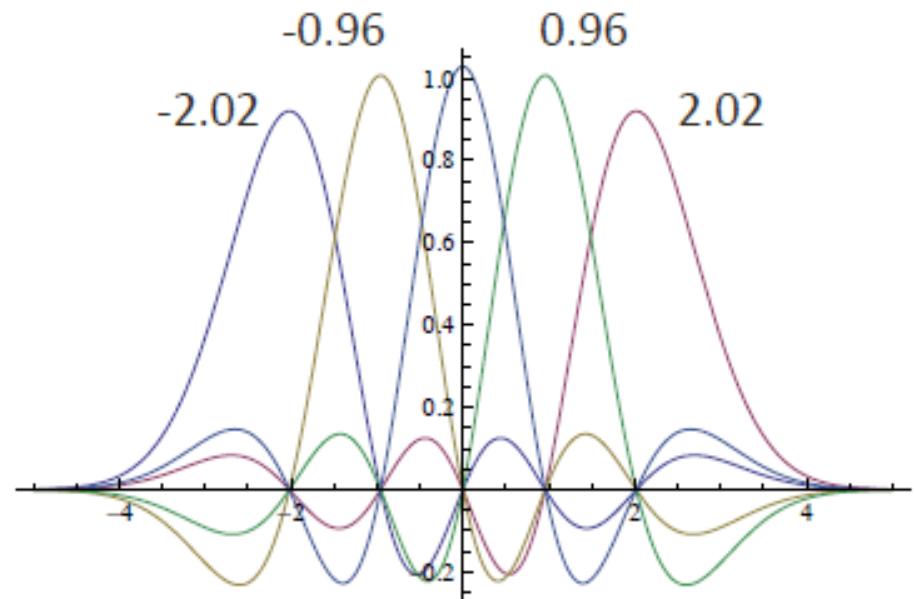
Rotations

- symmetric top eigenfunctions
- Wang functions

Discrete variable representation (DVR) basis functions



Hermite functions



Hermite-DVR functions

Basis functions

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

$$dV = \sin \Theta dR_1 dR_2 d\Theta$$

Direct product basis:  $\left\{ \chi_{n_1}(R_1) \chi_{n_2}(R_2) \Phi_\ell(\cos \Theta) \right\}_{n_1=0, n_2=0, \ell=0}^{N_1-1, N_2-1, L-1}$

Normalized Legendre-polynomials:

$$\text{Potential-optimized } \left(\frac{\partial^2}{\partial \Theta^2} + \text{ctg}(\Theta) \frac{\partial}{\partial \Theta} \right) \text{ basis } \Theta = \ell(\ell+1) P_\ell(\cos \Theta)$$

Angular singularity

DVR representation of the Hamiltonian

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

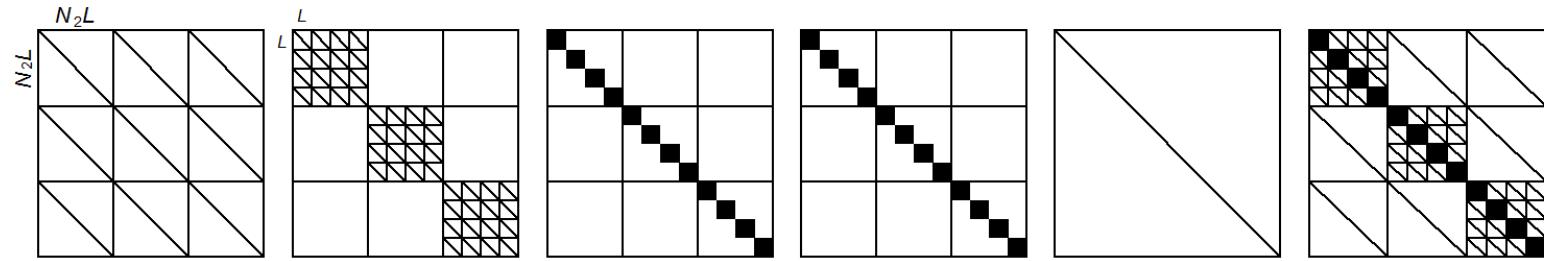
The diagram illustrates the derivation of matrix elements from the Hamiltonian. Arrows point from the terms in the Hamiltonian to their corresponding components in the matrices:

- $\frac{1}{2\mu_1} \frac{\partial^2}{\partial R_1^2}$ points to $(\mathbf{R}_j^{-2})_{n_j, n'_j} = \frac{1}{2\mu_j q_{n_j}^2} \delta_{n_j, n'_j}$
- $\frac{1}{2\mu_2} \frac{\partial^2}{\partial R_2^2}$ points to $(\mathbf{K}_\Theta)_{\ell, \ell'} = \mathbf{T}^+ \begin{pmatrix} 0.1 & 0 & \cdot & 0 \\ 0 & 1.2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & 0 \\ 0 & \cdot & 0 & (L-2)(L-1) \end{pmatrix} \mathbf{T}$
- $\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2}$ points to $(\mathbf{K}_{R_j})_{n_j, n'_j} = \langle \chi_{n_j}(R_j) \left| -\frac{1}{2\mu_j} \frac{\partial^2}{\partial R_j^2} \right| \chi_{n'_j}(R_j) \rangle$
- $\operatorname{ctg} \Theta \frac{\partial}{\partial \Theta}$ points to $(\mathbf{V}^{\text{diag}})_{n_1 n_2 \ell, n'_1 n'_2 \ell'} = V(q_{n_1}, q_{n_2}, q_\ell) \delta_{n_1 n_2 \ell, n'_1 n'_2 \ell'}$

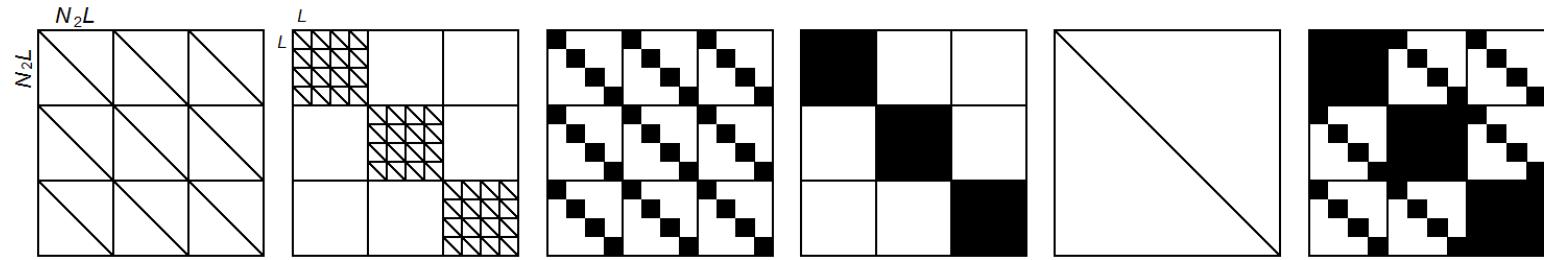
$$\mathbf{H}^{\text{DVR}} = \mathbf{K}_{R_1} \otimes \mathbf{I}_{R_2} \otimes \mathbf{I}_\Theta + \mathbf{I}_{R_1} \otimes \mathbf{K}_{R_2} \otimes \mathbf{I}_\Theta + \mathbf{R}_1^{-2} \otimes \mathbf{I}_{R_2} \otimes \mathbf{K}_\Theta + \mathbf{I}_{R_1} \otimes \mathbf{R}_2^{-2} \otimes \mathbf{K}_\Theta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

Sparse matrix \rightarrow Special iterative Lanczos „diagonalization”

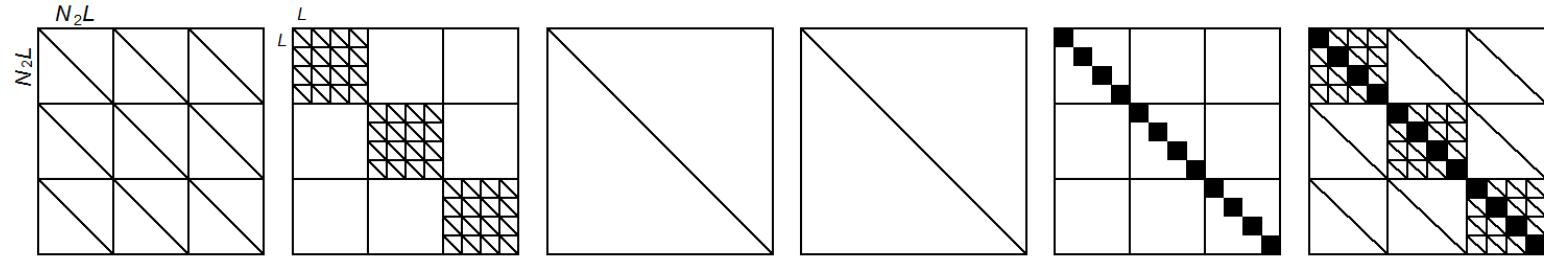
D³OPI



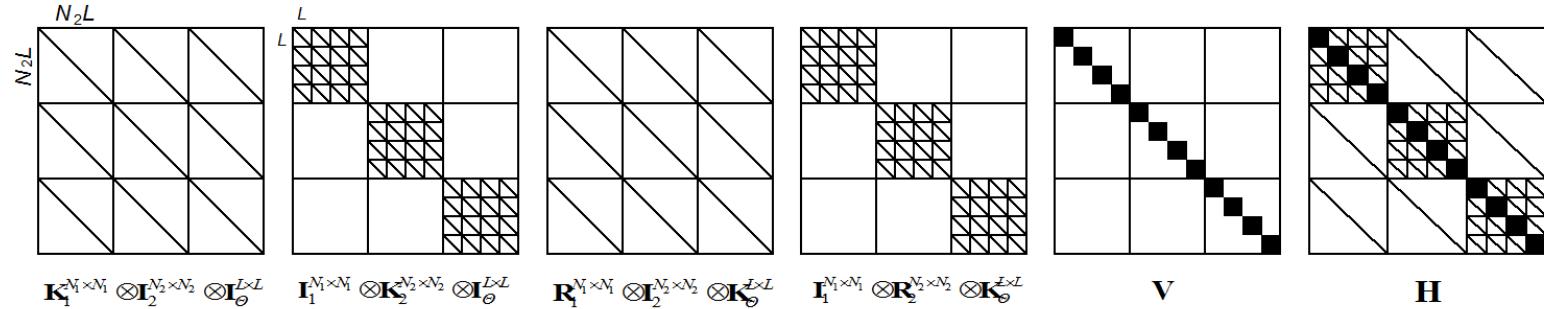
ED³OPI



D²FOPI

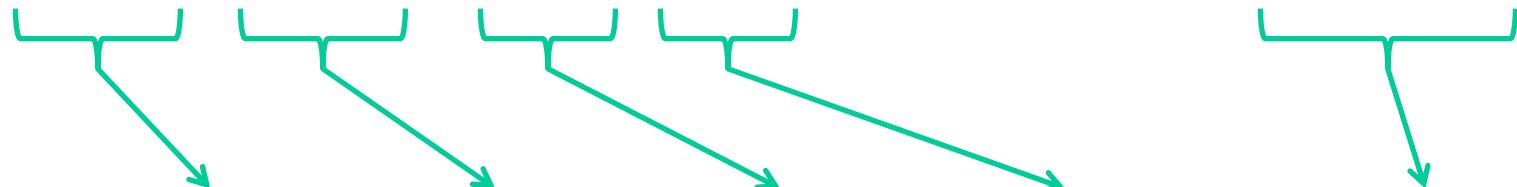


ED²FOPI



Hamiltonian matrix in case of the D²FOPI algorithm

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



A sum of five sparse matrices representing the decomposed Hamiltonian. The matrices are arranged horizontally with plus signs between them. The first matrix is a complex pattern of black and white squares. The second matrix has diagonal black lines. The third matrix has a central block of black and white squares. The fourth matrix has diagonal black lines. The fifth matrix has a central block of black and white squares. All matrices are 100x100.

$$N_1 = 105$$

$$N_2 = 100$$

$$L = 80$$



99,94% nulla elem

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

- Spectral convergence of the quadrature discretization method in the solution of the Schrodinger and Fokker-Planck equations: Comparison with sinc methods (J. Chem. Phys., 2006.)
- "Lagrange functions": A family of powerful basis sets for real-space order-N electronic structure calculations (Phys. Rev. Lett., 2004.)
- Semiclassical generalization of the Darboux-Christoffel formula (J. Math. Phys., 2002.)
- The unexplained accuracy of the Lagrange-mesh method (Phys. Rev. E, 2002.)
- Quantum theory of bimolecular chemical reactions (Reports on Progress in Physics, 2000.)
- Integrals of Lagrange functions and sum rules (J. Phys. A-Math. and Theo., 2011.)
- Vortex formation in a rotating two-component Fermi gas (Phys. Rev. A, 2011.)
- Implementation of the time-dependent configuration-interaction singles method for atomic strong-field processes (Phys. Rev. A, 2010.)
- Discrete Variable Representation Implementation of the One-Electron Polarization Model (J Chem. Theo. and Comp., 2010.)
- Grid method for computation of generalized spheroidal wave functions based on discrete variable representation (Phys. Rev. E., 2009.)
- Variational estimates using a discrete variable representation (Phys. Rev. A, 2004.)
- The Bloch wave operator: generalizations and applications: II. The time-dependent case (J. Phys. A-Math and Gen., 2003.)
- Wave packet dynamics on the repulsive potential surface of BaFCH₃ excited at 745 nm (Chem. Phys. Lett., 2002.)
- Analysis of the R-matrix method on Lagrange meshes (J. Phys. B-At. Mol. and Opt. Phys., 1998.)
- The influence of surface motion on the direct subsurface absorption of H-2 on Pd(111) (J. Chem. Phys., 1997.)
- Matrix-free application of Hamiltonian operators in Coifman wavelet bases (J. Chem. Phys., 2010.)
- Phase diagram of the rotating two-component Fermi gas including vortices (arXiv:1201.2856, 2012)
- Variational discrete variable representation for excitons on a lattice (Phys. Rev. B, 2011.)
- Photoionization cross sections of hydrogen impurities in spherical quantum dots using the finite-element discrete-variable representation (Phys. Rev. A, 2011.)

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)
- Inefficient for non-orthogonal coordinate systems

Transformation between DVR and FBR is quick & simple for standard DVR

Diagonalization of large matrices

1.) Secular equation with metric \mathbf{S}

$$\mathbf{A}\mathbf{v}^K = \lambda^K \mathbf{S}\mathbf{v}^K$$

2.) Secular equation with metric $\mathbf{S} = \mathbf{I}$

$$\mathbf{A}\mathbf{U} = \mathbf{U}\mathbf{D} \quad \mathbf{A} = \mathbf{U}\mathbf{D}\mathbf{U}^T$$

3.) Jacobi method (1846)

$$\mathbf{A} = \mathbf{U}^+ \mathbf{A}_{n \times n}^{(0)} \mathbf{U}$$

\mathbf{U} : product of a large no. of simple, unitary matrices

$$\mathbf{U} = \lim_{k \rightarrow \infty} \mathbf{R}^{(k)} \mathbf{R}^{(k-1)} \mathbf{R}^{(k-2)} \dots \mathbf{R}^{(0)}$$

$$\tau^2(\mathbf{A}) = \sum_{p>q} A_{pq}^2 \quad \text{nondiagonality measure}$$

Diagonalization of large matrices

- 4.) Givens (1954): tridiagonal form in $0.5(n - 1)(n - 2)$ rotations
- 5.) Householder: much improved tridiagonalization
- 6.) Wilkinson: QL (sometimes called QR) algorithm,
applicable after tridiagonalization
- 7.) non-unit metric: Cholesky decomposition (Gram-Schmidt
in disguise), canonical or Löwdin (symmetric) orthogonalization

Iterative Lanczos „diagonalization”

$$\mathbf{B}^T \mathbf{A} \mathbf{B} = \begin{pmatrix} d_1 & t_1 & \cdot & \cdot & \cdot \\ t_1 & d_2 & t_2 & \cdot & \cdot \\ \cdot & t_2 & d_3 & t_3 & \cdot \\ \cdot & \cdot & t_3 & d_4 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{pmatrix} = \mathbf{T} \quad \text{A large, B small}$$

$$\mathbf{A}\mathbf{b}_i = t_{i-1}\mathbf{b}_{i-1} + d_i\mathbf{b}_i + t_i\mathbf{b}_{i+1}$$

start: \mathbf{x}_1

$$\mathbf{b}_i = \mathbf{x}_i / x_i$$

Krylov sequence:

$$\mathbf{x}_1, \mathbf{Ax}_1, \mathbf{A}^2\mathbf{x}_1, \dots$$

$$\boldsymbol{\sigma}_i = \mathbf{Ab}_i$$

$$d_i = \boldsymbol{\sigma}_i^T \cdot \mathbf{b}_i$$

preconditioning

$$\mathbf{x}_{i+1} = \boldsymbol{\sigma}_i - d_i \mathbf{b}_i - t_{i-1} \mathbf{b}_{i-1}$$

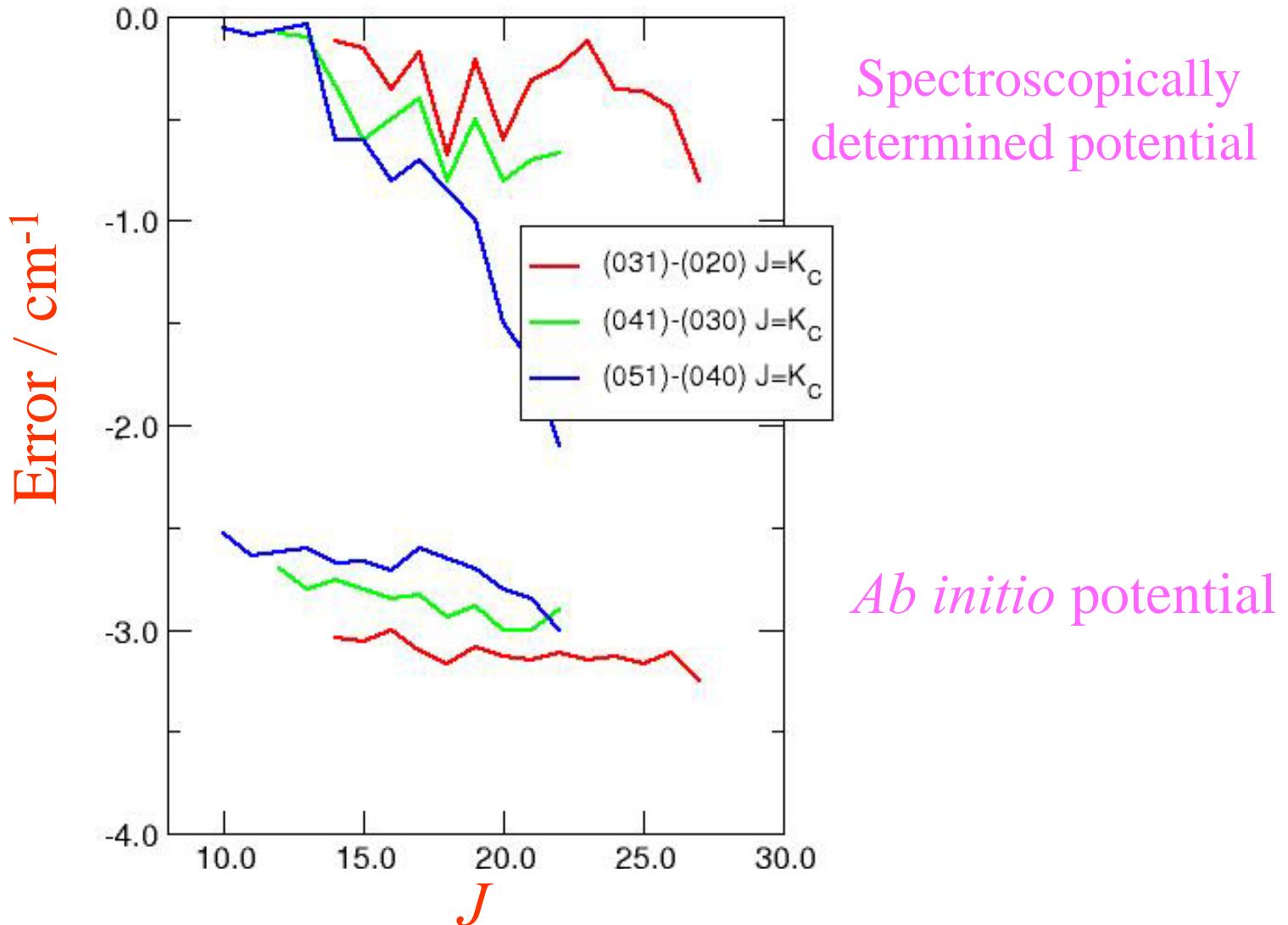
$$t_i = x_{i+1}$$

Question 1:

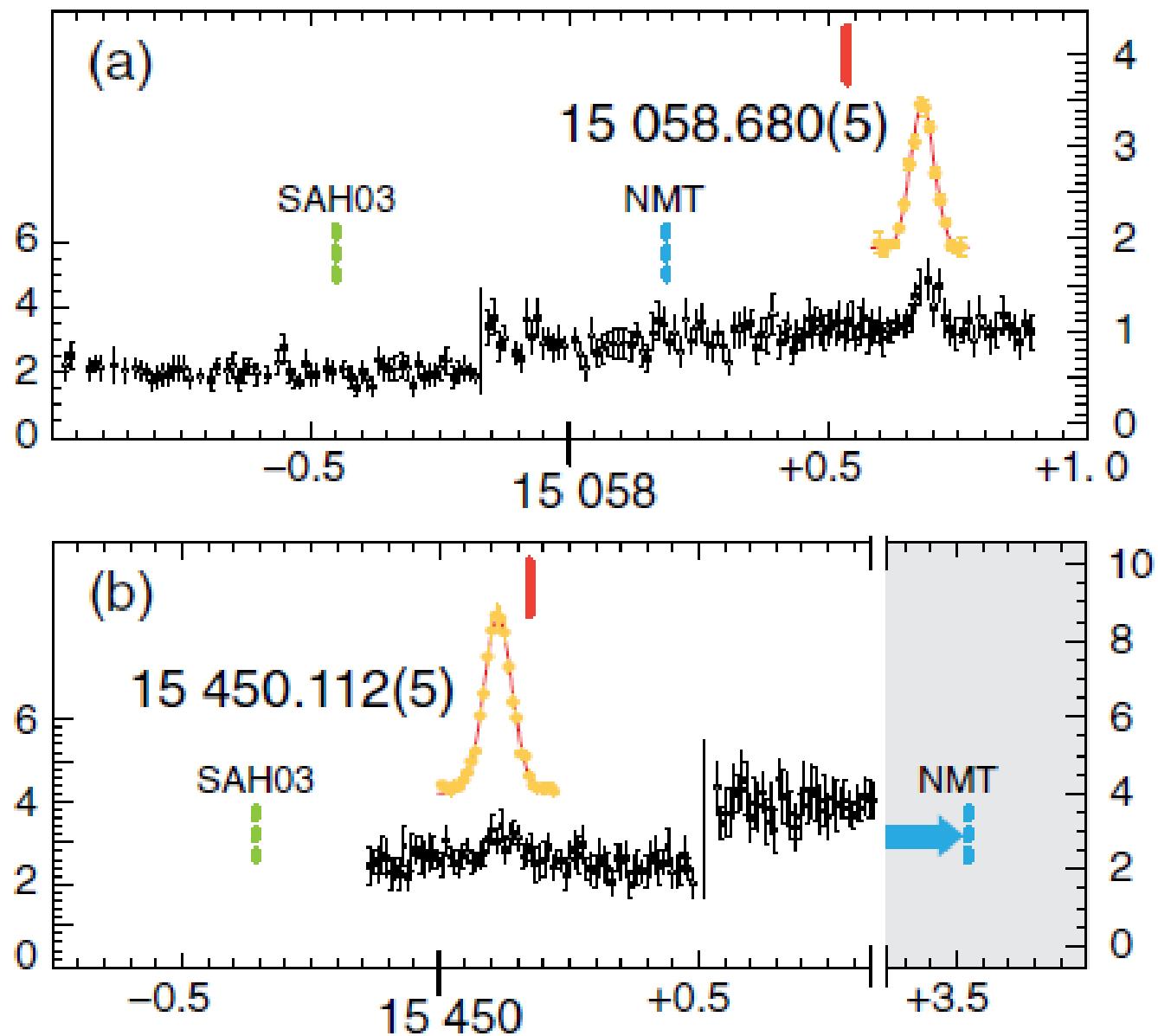
**Can experimental precision
be achieved for the
first-principles prediction of
high-resolution
rotational-vibrational spectra
of polyatomic molecules?**

Disadvantages of empirical fitting

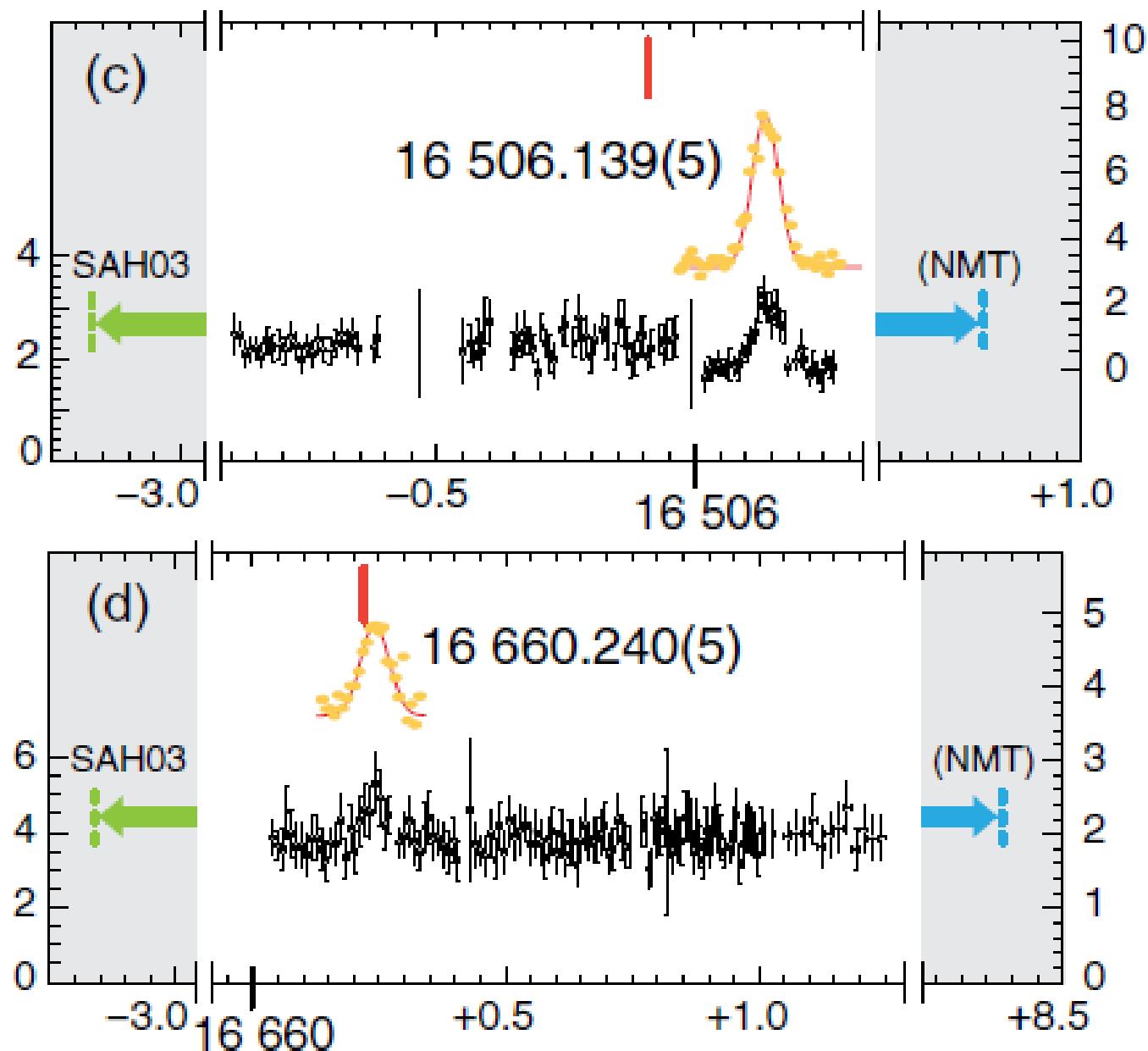
Assignments using branches



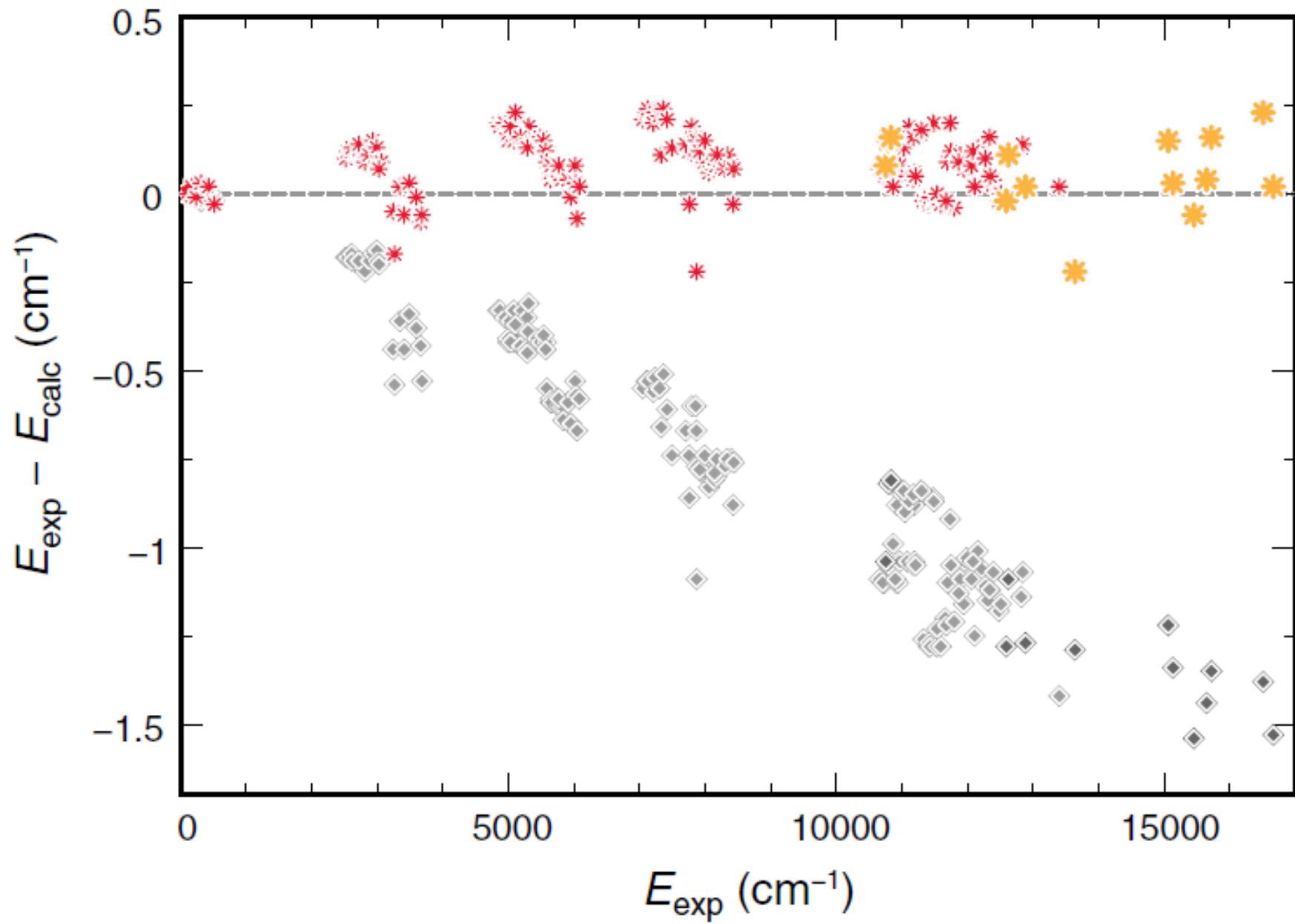
The color of H_3^+ (*PRL* 2012, 108, 023002)



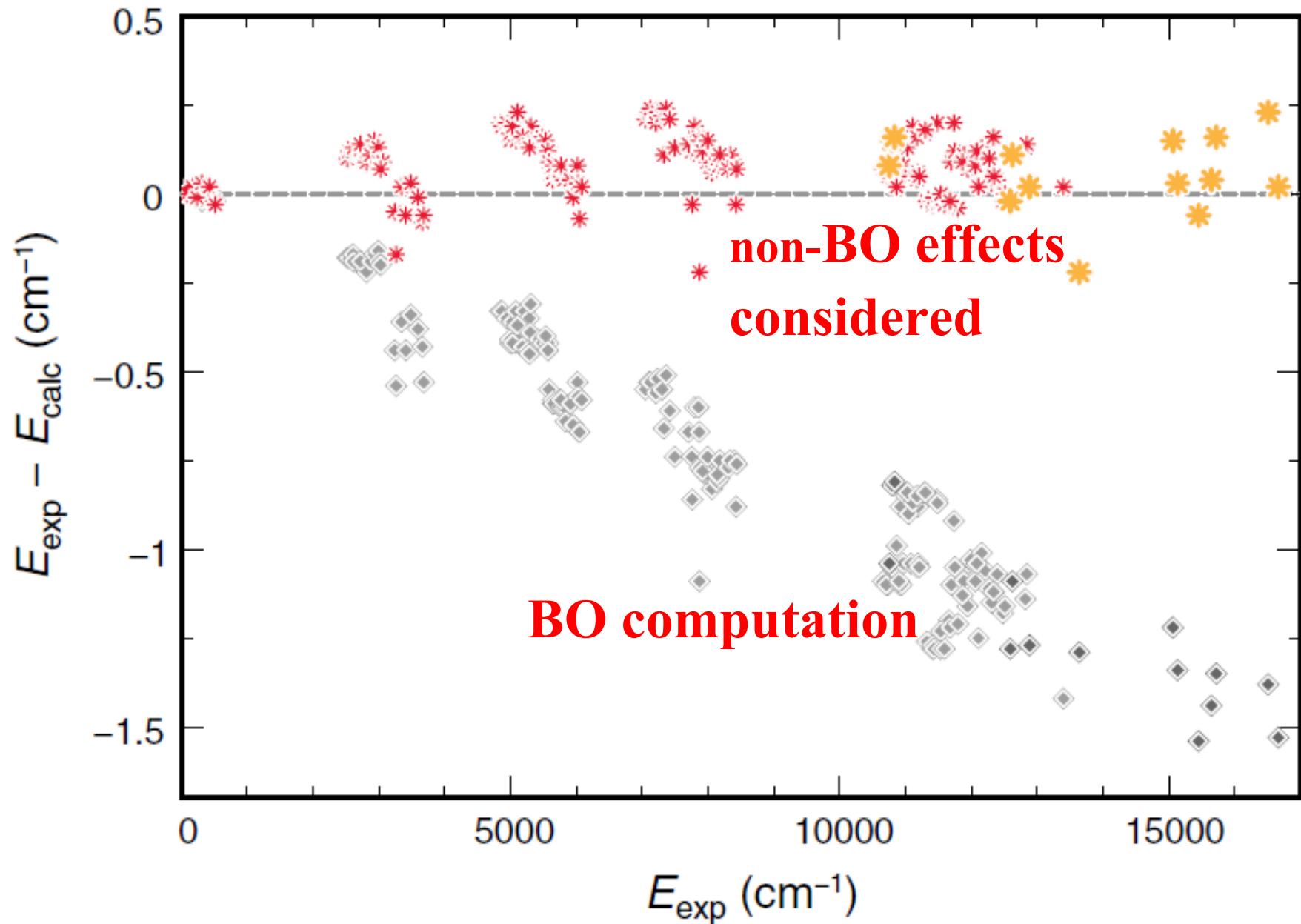
The color of H_3^+ (*PRL* 2012, 108, 023002)



Deviation between experiment and theory for H_3^+



Deviation between experiment and theory for H_3^+

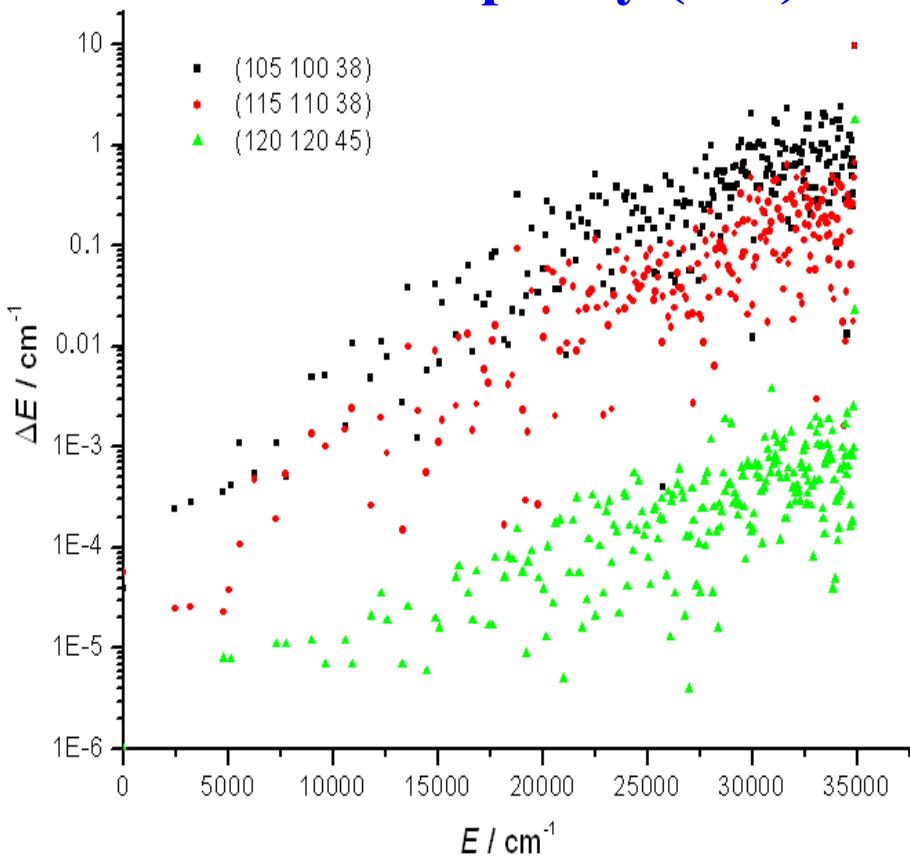


Question 2:

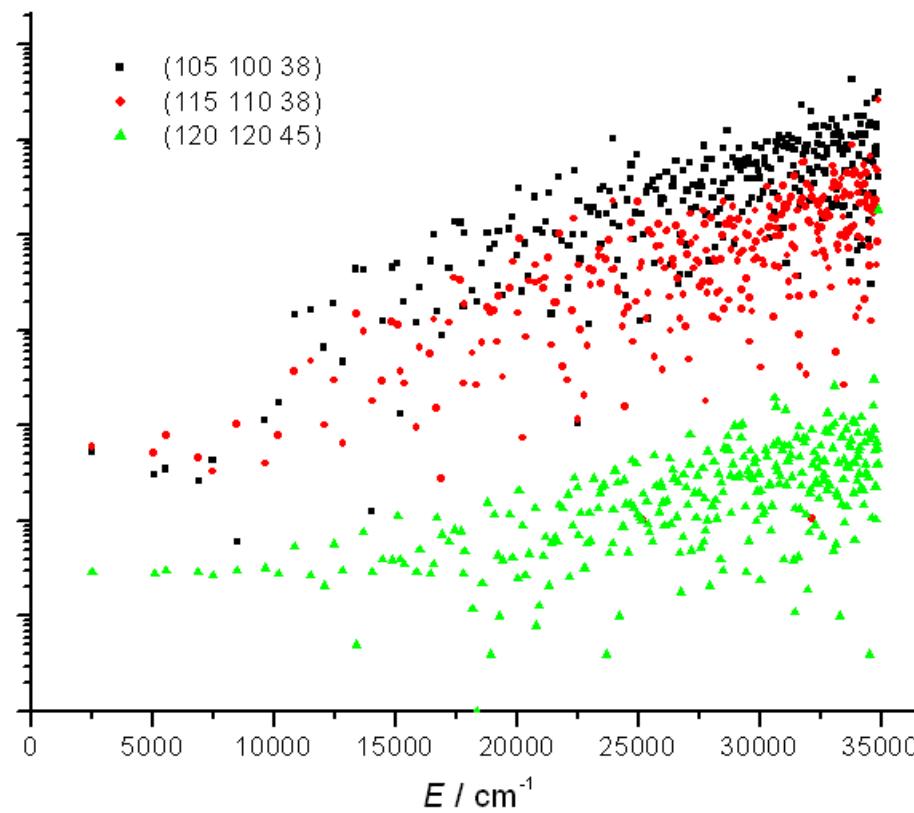
Can complete high-resolution rotational-vibrational spectra (all the bound states) of polyatomic molecules be computed *ab initio* in a converged way?

Complete vibrational spectroscopy of H_3^+

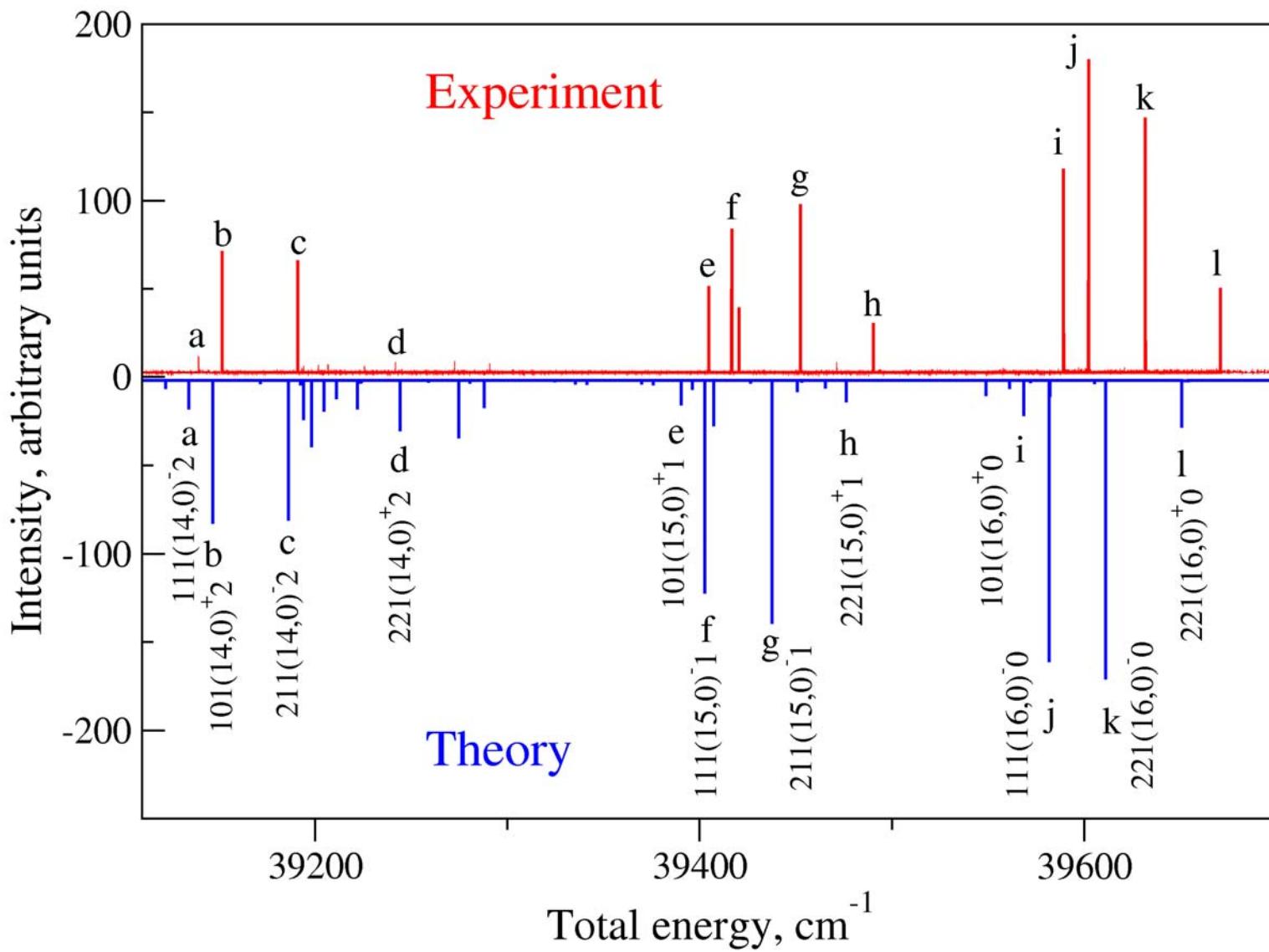
even parity (688)



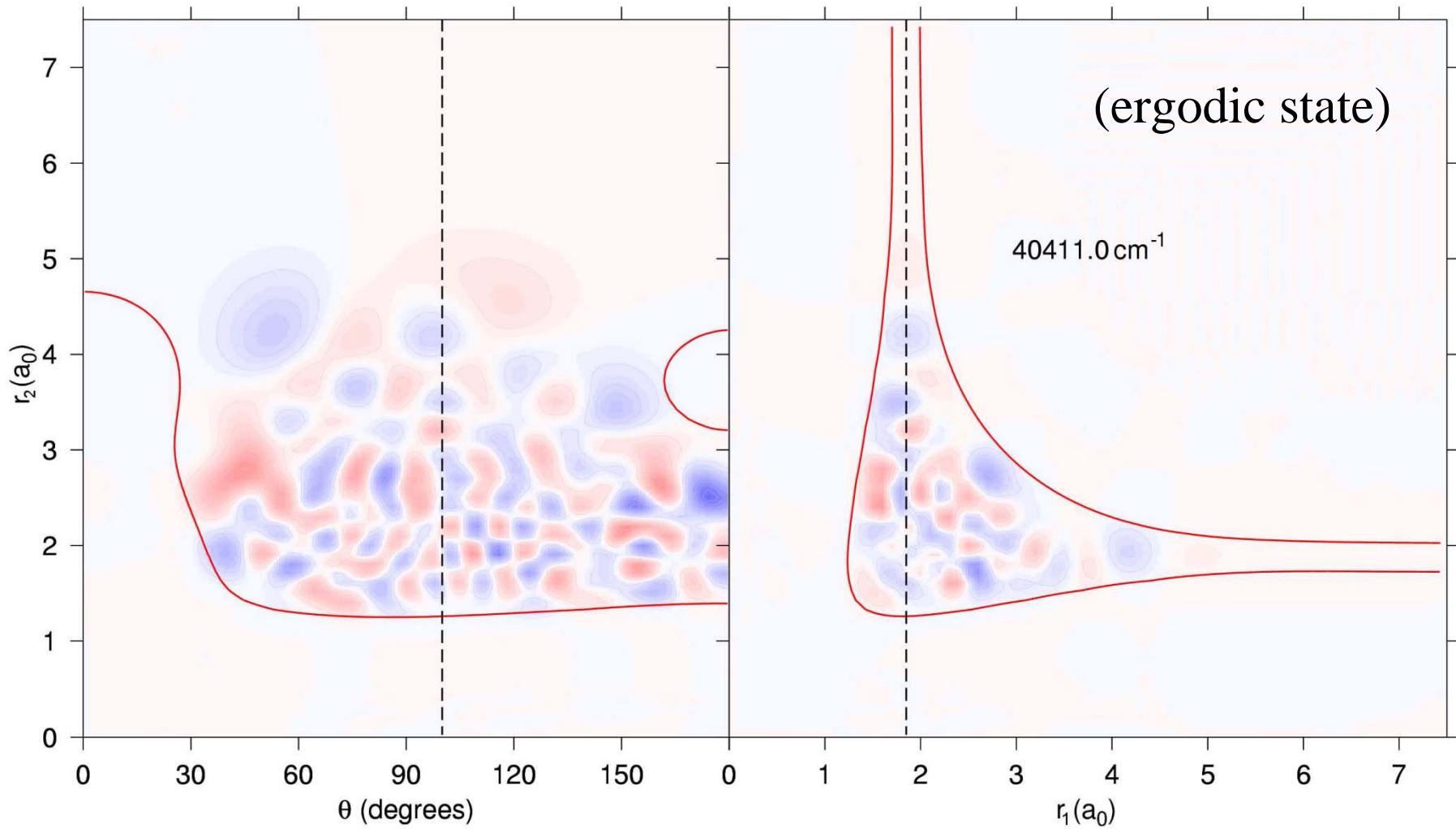
odd parity (599)



Bound rovibrational states of water under the dissociation limit

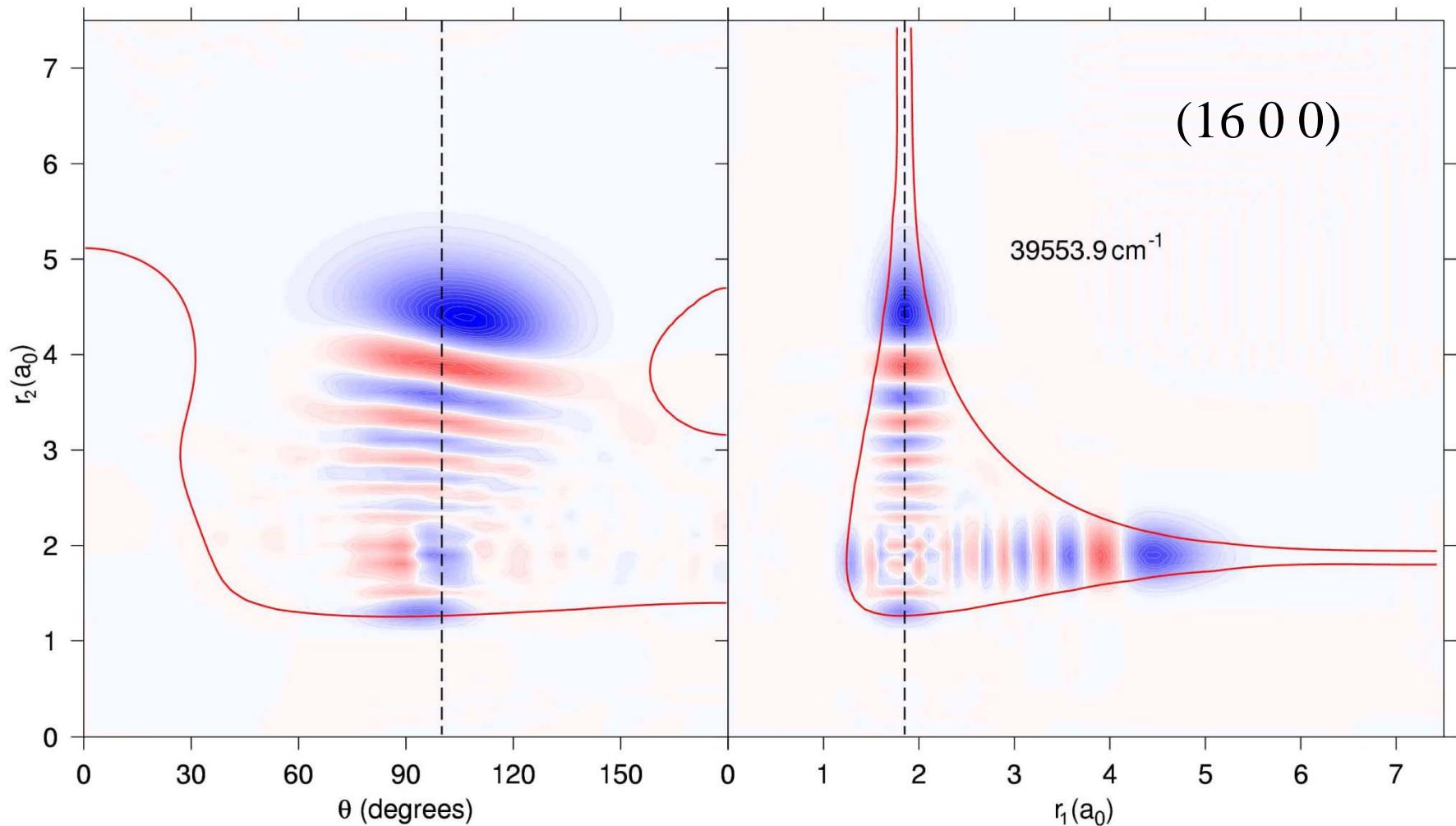


Highly excited vibrational states of water

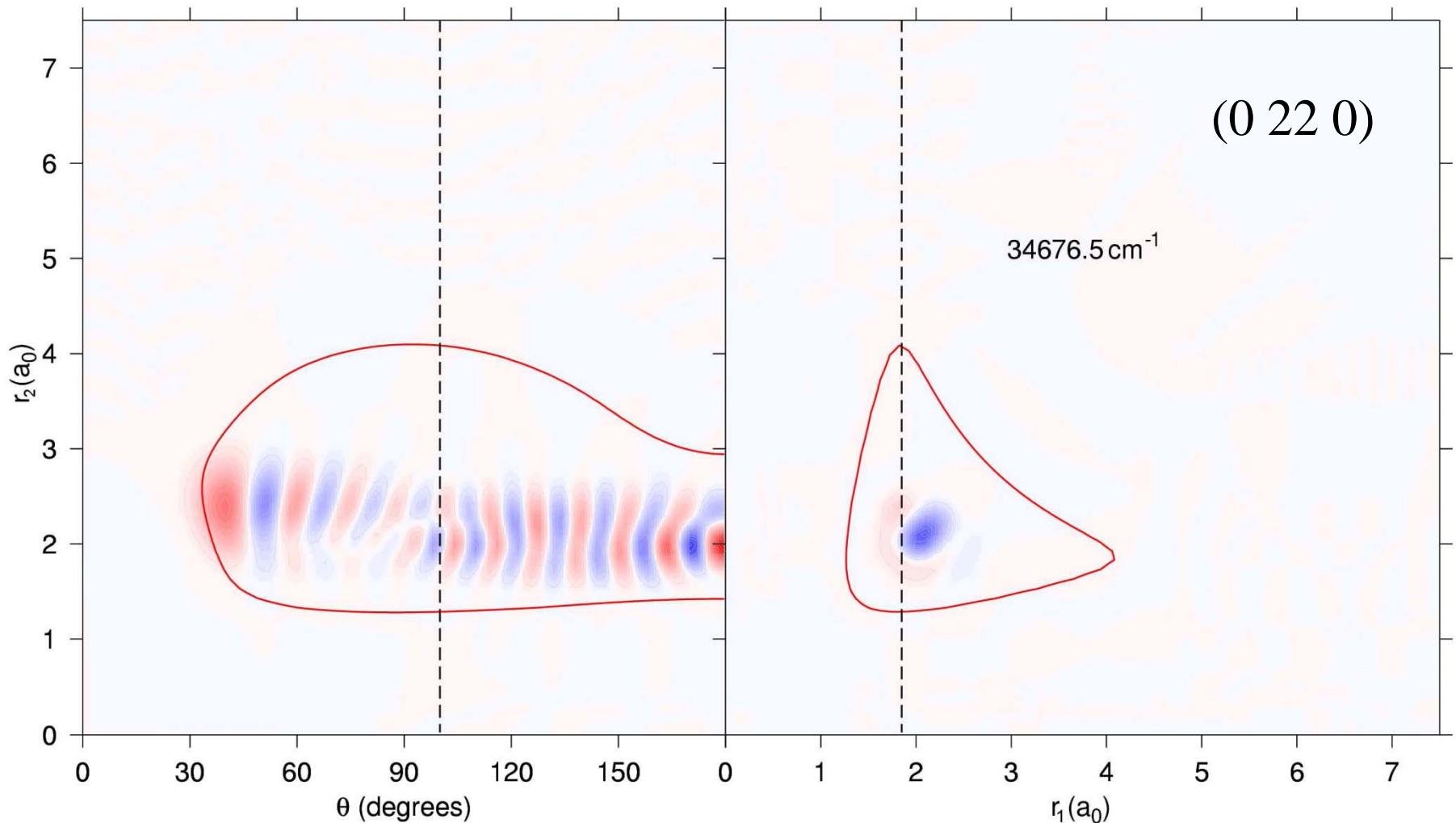


A. G. Császár *et al.*, *J. Quant. Spectr. Rad. Transfer* **111**, 1043 (2010).

Highly excited vibrational states of water



Highly excited vibrational states of water



Question 3:

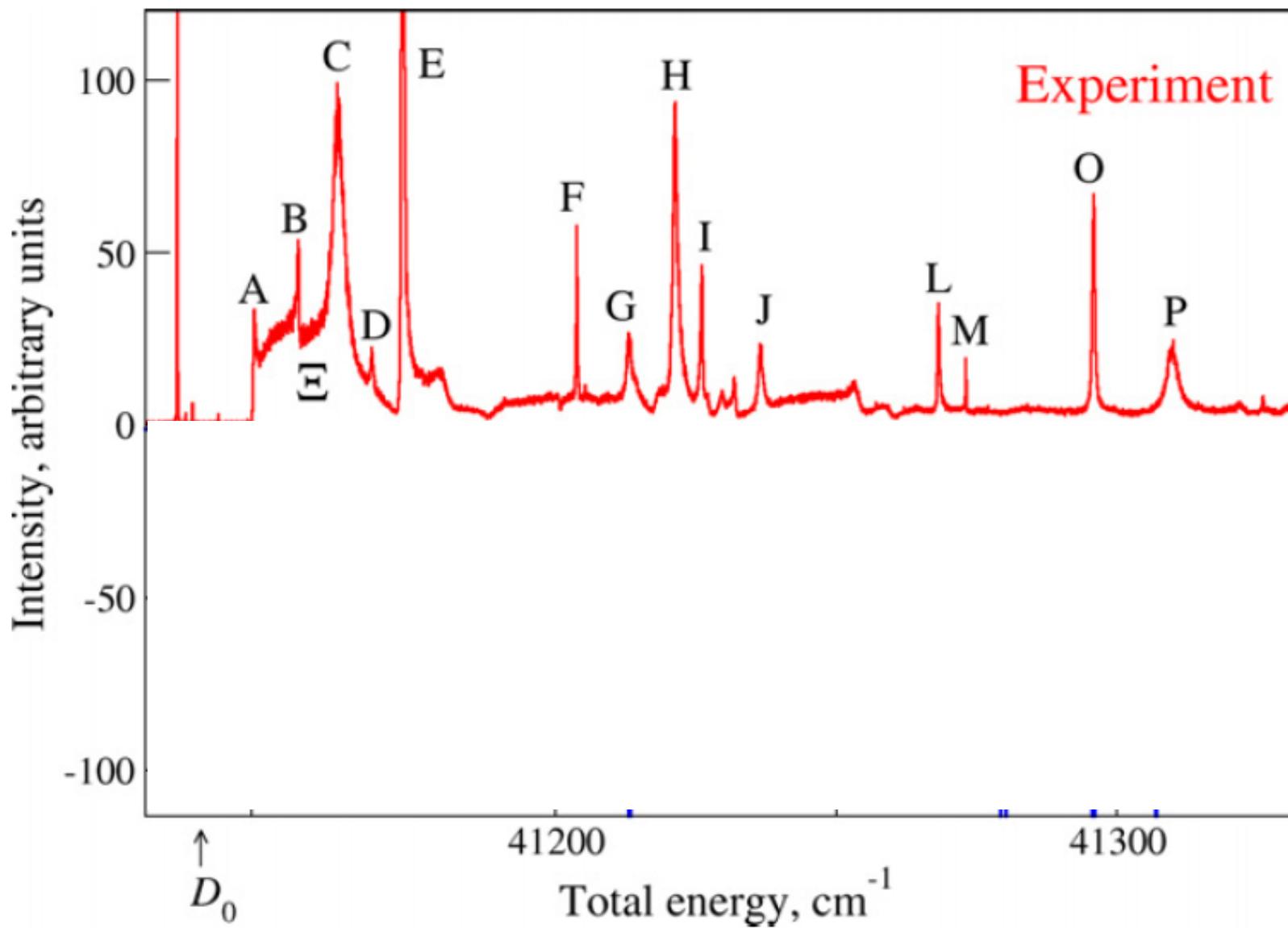
**How do
rotational-vibrational spectra
of polyatomic molecules
beyond the first dissociation limit
look like?**

Resonance states are stationary eigenstates of the Hamiltonian which are associated with ...

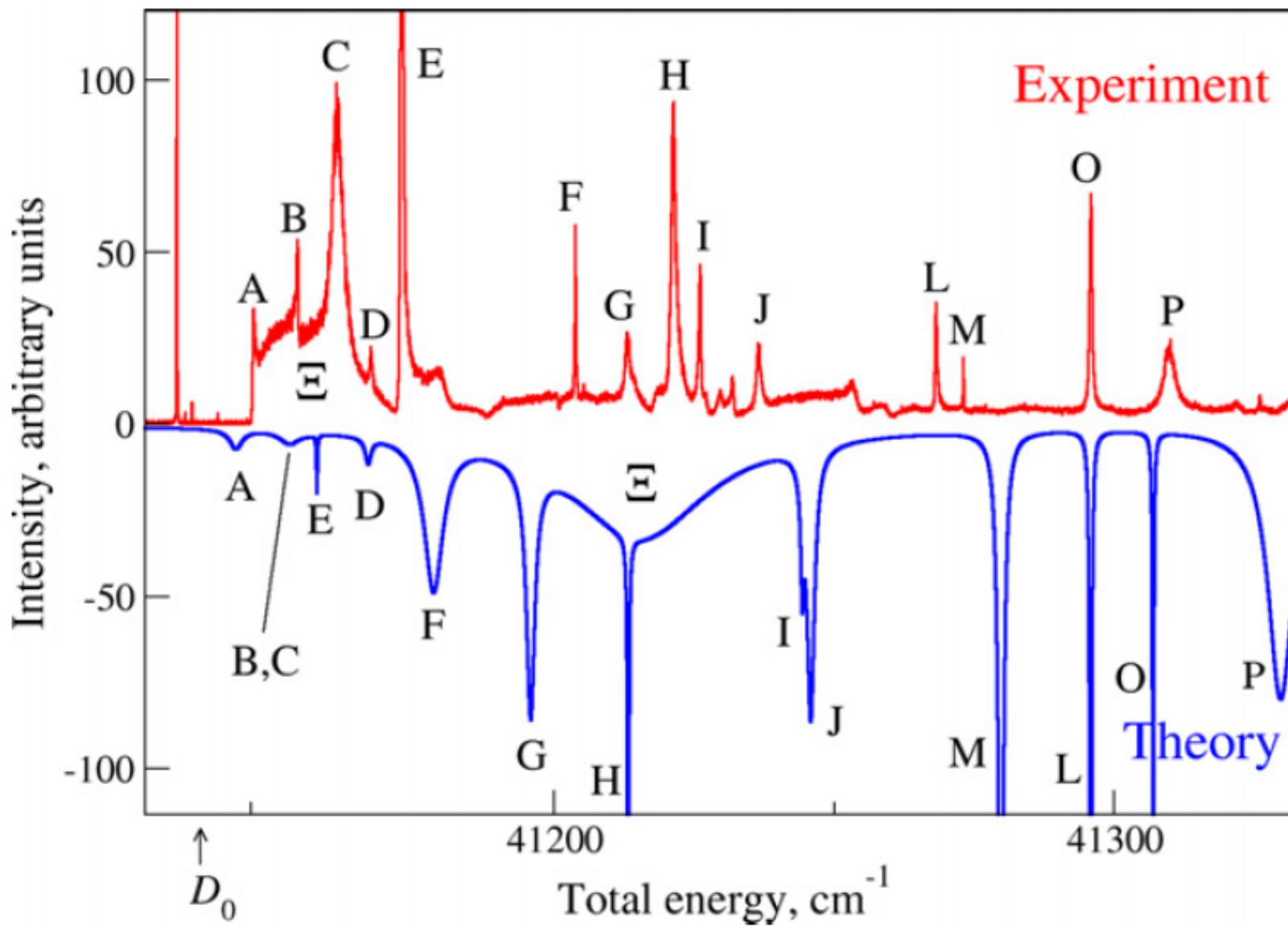
- complex, discrete eigenvalues of the Hamiltonian of the form: $E = E_0 - i \frac{\Gamma}{2}$ where E_0 is the energy and Γ is related to the lifetime
- wavefunctions that are not in L^2 and which diverge exponentially with respect to the dissociation coordinate(s)

There are two possibilities to compute Feshbach and shape resonances: CAP and complex scaling

Quasibound states of water beyond the dissociation limit



Quasibound states of water beyond the dissociation limit



Question 4:

How high in energy do the simple rigid-rotor and harmonic-oscillator pictures with their corresponding approximate RRHO quantum numbers work?

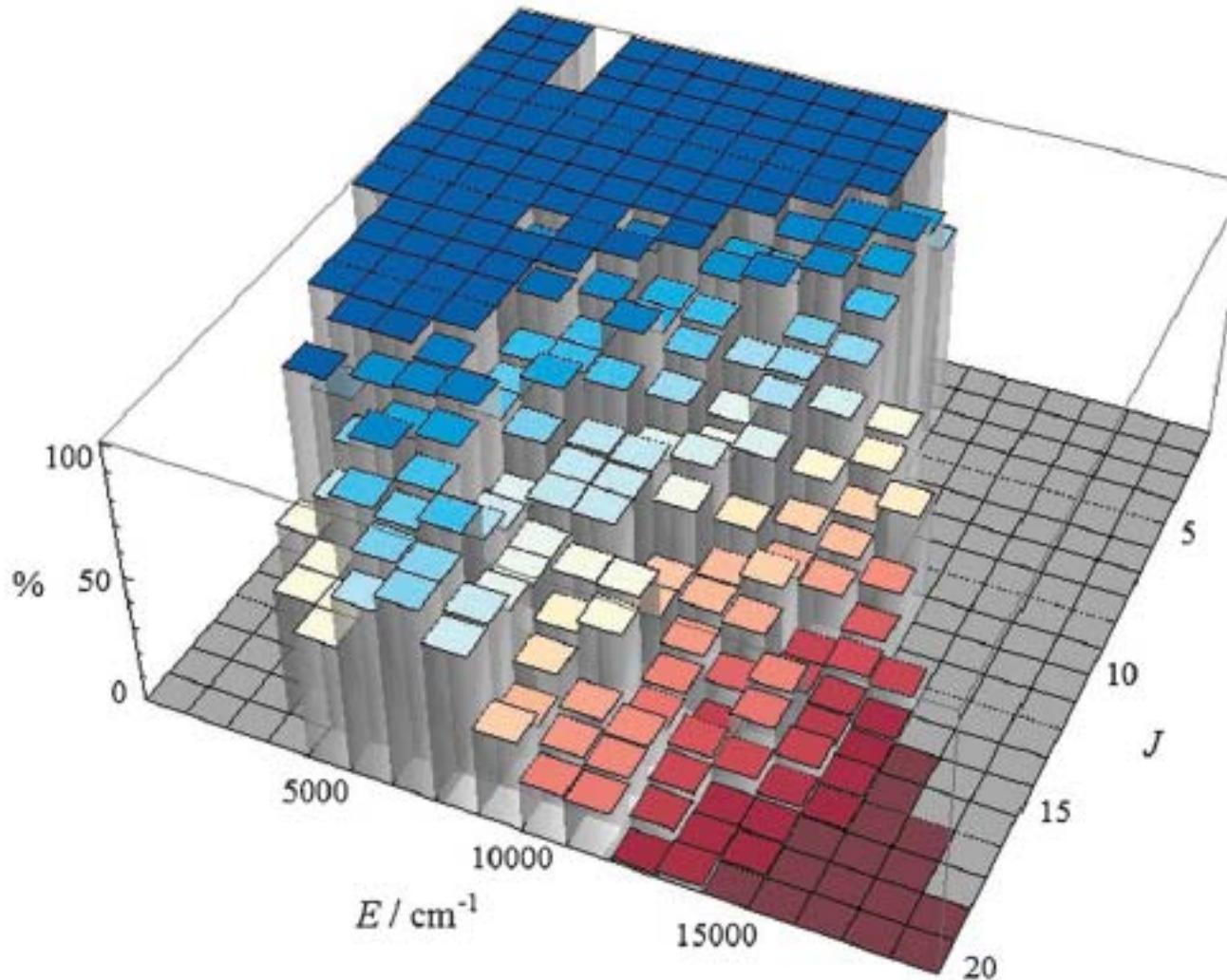
Normal Mode Decomposition (NMD)

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

HNCO

„Fundamentals“

Percentage of clearly identifiable rovibrational states of H_2^{16}O based on RRD coefficients



Question 5:

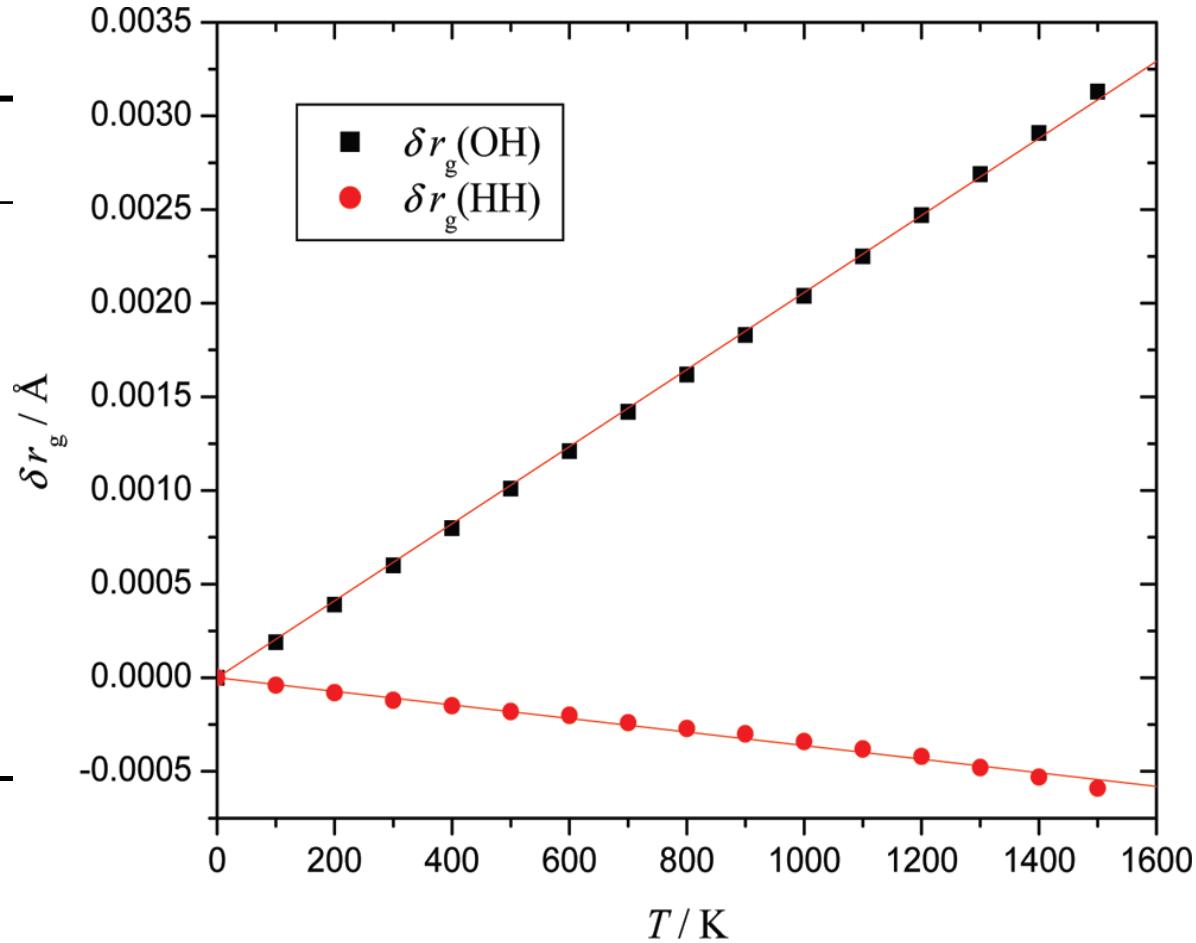
Can quantum chemistry predict measurable, *i.e.*, temperature-dependent, rovibrationally averaged molecular properties?

r_g structures of water ($T = 293$ K)

	$H_2^{16}O$		$D_2^{16}O$	
	$r_g(OH)/\text{\AA}$	$r_g(HH)/\text{\AA}$	$r_g(OD)/\text{\AA}$	$r_g(DD)/\text{\AA}$
r_g calc.	0.97566	1.53812	0.97136	1.53122
(GED)	(0.9763)	(1.567)	(0.9700)	(1.526)
(Spectr.)	(0.9745)	(1.537)	(0.9702)	(1.531)
r_a calc.	0.97138	1.52956	0.96783	1.52516
(Adiabatic r_e)	0.95785	1.51472	0.95783	1.51460
$r_g - r_e$	0.01781		0.01353	
	(0.0182) ^{cubic}		(0.0131) ^{cubic}	

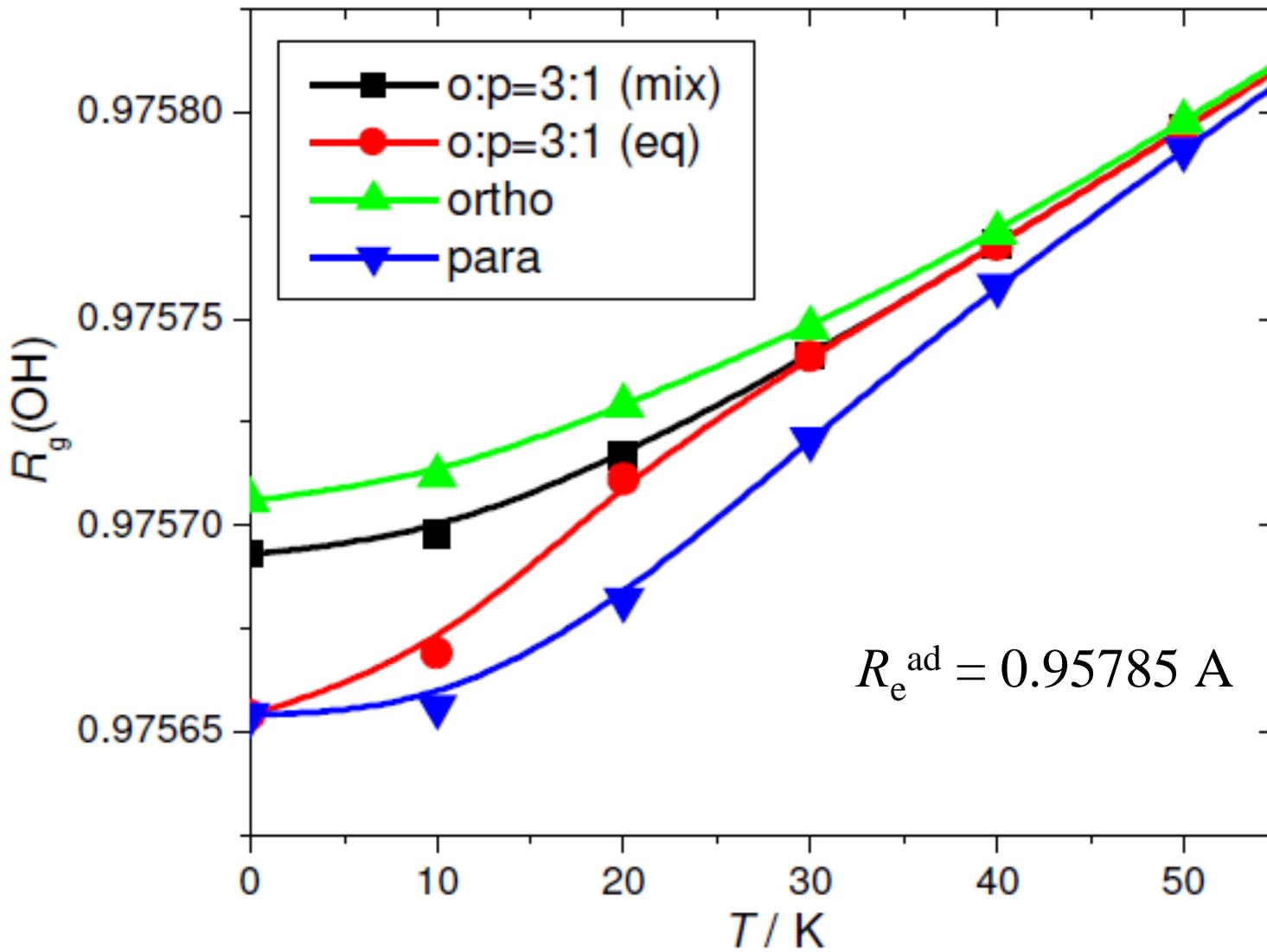
Temperature dependence of $r_g(\text{OH})$ of water

H_2^{16}O	
	$r_g(\text{OH})/\text{\AA}$
0 K	0.97565
300 K	0.97625
700 K	0.97718
1000 K	0.97813
1500 K	0.98048



G. Czakó, E. Mátyus, A. G. Császár, *J. Phys. Chem. A* **113**, 11665 (2009).

Effective structures of ortho- and para-water



Summary

- (a) DOPI-type procedures, using tailor-made kinetic energy operators, are the favored techniques for the solution of the (tri- and tetra-atomic) variational rovibrational problem when the goal is to match experiments, compute full rovibrational spectra (including resonances), or estimate rovibrational averages.
- (b) Molecules have quasibound states above the dissociation limit, their computation is feasible via fourth-age quantum chemical techniques.
- (c) Spin statistics play an important for molecular spectroscopy.
- (d) There is still a lot to learn about nonadiabatic behavior of small molecules if full understanding of molecular spectra is desired.
- (e) Variational nuclear motion computations can bridge the gap between equilibrium properties computed via electronic structure computations and temperature-dependent, rovibrationally averaged measured molecular properties.