

Vibrational spectroscopy beyond the harmonic approximation

September 25, 2007

Motivation

- Determine whether minimum or saddle point found
- Calculation of zero point energy
 - Important for relative energies
 - Calculating reaction barriers
- Vibrational partition function for entropic contributions to free energy
- Aid in geometry optimisations
- Experimental observables
 - Infrared/Raman frequencies and intensities
 - Vibrational dynamics and photochemistry

Harmonic Oscillator

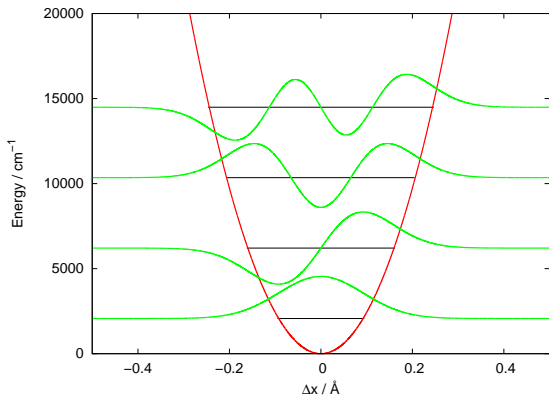
- Virtually all quantum chemistry programs can calculate normal mode (harmonic) vibrational frequencies
 - Gaussian, Molpro, Turbomole, Dalton, Gamess ...
- The normal mode picture is based upon the harmonic oscillator

$$\hat{H} = -\frac{1}{2}g_{ii}p_i^2 + \frac{1}{2}F_{ii}x_i^2$$

$$E/hc = \left(\nu + \frac{1}{2}\right)\tilde{\omega} \quad \tilde{\omega} = \frac{1}{2\pi c} \sqrt{F_{ii}g_{ii}}$$

$$f \propto \langle e|\vec{\mu}|g\rangle^2 \quad \vec{\mu} \approx \frac{d\mu}{dx}$$

Harmonic Oscillator



For HF with $\tilde{\omega}=4139.9 \text{ cm}^{-1}$

Results

hydrogen fluoride (HF)				
Method	Harmonic freq.	Obs. freq.	HOLD f	Expt f
Hartree-Fock	4471.8		164.3	
MP2	4137.4	3961.4	122.5	94.4
CCSD(T)	4139.9			
carbon monoxide (CO)				
Hartree-Fock	2426.6		144.6	
MP2	2123.4	2143.3	36.5	60.2
CCSD(T)	2159.7			

- All calculations with the aug-cc-pVQZ basis set
- Frequencies in cm^{-1} , f in km mol^{-1}

Scaling Factors

16502

J. Phys. Chem. **1996**, *100*, 16502–16513

Harmonic Vibrational Frequencies: An Evaluation of Hartree–Fock, Møller–Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors

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Received: April 2, 1996; In Final Form: July 30, 1996[®]

- cited 2800 times!
- s.f. = ω_o/ω_c
- A list of scaling factors available at <http://srdata.nist.gov/cccbdb/vsf.asp>

Scaling Factors

hydrogen fluoride (HF)			
Method	Harmonic freq.	Obs. freq.	s.f.
Hartree-Fock	4471.8		0.886
MP2	4137.4	3961.4	0.957
CCSD(T)	4139.9		0.957
carbon monoxide (CO)			
Hartree-Fock	2426.6		0.883
MP2	2123.4	2143.3	1.009
CCSD(T)	2159.7		0.992

- Problem - we are correcting for two effects with one scaling factor
 - Deficiency in our ab initio method
 - Anharmonicity

Anharmonicity

- Vibrations are not harmonic
- For a diatomic we can just choose a different potential
 - Morse potential $V(x) = D[1 - e^{-ax}]^2$

$$E/hc = (v + \frac{1}{2})\tilde{\omega} - (v + \frac{1}{2})^2\tilde{\omega}_x$$

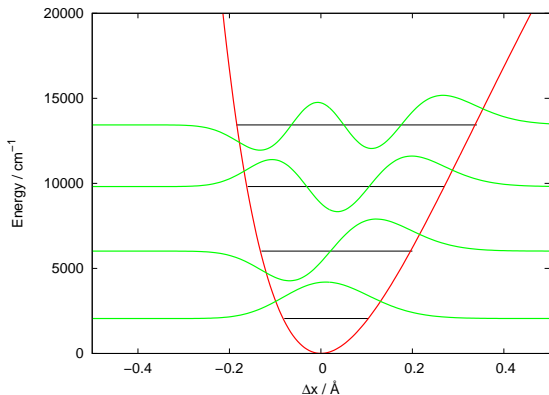
- Taylor/Maclaurin series

$$V(x) = V(0) + \frac{d^2V}{dx^2} \frac{x^2}{2} + \frac{d^3V}{dx^3} \frac{x^3}{6} + \frac{d^4V}{dx^4} \frac{x^4}{24} + \dots$$

$$V(x) = V(0) + \frac{1}{2}F_{ii}x^2 + \frac{1}{6}F_{iii}x^3 + \frac{1}{24}F_{iv}x^4 + \dots$$

- Numerical solution of 'exact' potential

Anharmonic Oscillator



HF calculated with CCSD(T)/aug-cc-pVQZ



Results

Hydrogen Fluoride (HF)				
Method	Harmonic	Δ	Anharmonic	Observed
Hartree-Fock	4471.8	165.6	4306.2	
MP2	4137.4	172.0	3965.4	3961.4
CCSD(T)	4139.9	174.7	3965.2	
Carbon Monoxide (CO)				
Hartree-Fock	2426.6	23.0	2403.6	
MP2	2123.4	27.0	2096.4	2143.3
CCSD(T)	2159.7	25.7	2134.0	

- Anharmonic values found by numerically solving the 1D Schrödinger equation

Results

Hydrogen Fluoride (HF)			
Method	HOLD	Anharmonic	Observed
Hartree-Fock	164.3		
MP2	122.5		94.4
CCSD(T)		100.8	
Carbon Monoxide (CO)			
Hartree-Fock	144.6		
MP2	36.5		60.2
CCSD(T)		64.0	

- Anharmonic values found by numerically solving the 1D Schrödinger equation and numerically integrating $\langle e|\vec{\mu}|g\rangle$

A note of caution

- As for all ab initio calculations, sometimes we can get the right answer for the wrong reasons
- We need to have a realistic view of the accuracy of our calculated frequencies

Normal Modes

- For a polyatomic molecule

$$V = V(0) + \sum_i \left(\frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 x_i x_j + \dots$$

Electronic energy Gradient Hessian

- $V(0)$ does not affect vibrations and at a stationary point the gradient is zero. If we keep to harmonic oscillators

$$V = \frac{1}{2} \sum_{i,j} F_{ij} x_i x_j \quad F_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0$$

Normal Modes

- To simplify the problem we use mass-weighted coordinates

$$q_i = \sqrt{m_i} x_i$$

- The potential then becomes

$$V = \frac{1}{2} \sum_{i,j} K_{ij} q_i q_j \quad K_{ij} = \frac{F_{ij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0$$

- Normal coordinates Q_i are linear combinations of the mass-weighted coordinates q_i such that the total energy is diagonal i.e. no cross terms

$$V = \frac{1}{2} \sum_i \kappa_i Q_i^2$$

Normal Modes

- To calculate the harmonic frequencies we need the Hessian (second derivative of the potential energy with respect to the coordinates)
- Some methods have analytical Hessians
 - HF, DFT, MP2, CIS and CASSCF
- otherwise we have to calculate the Hessian numerically 😞
 - CCSD, CCSD(T)

Normal Modes

- In Gaussian a frequency calculation is requested with the keyword `FREQ`
- Frequency calculations are only physically meaningful at stationary points, so often we combine optimisation and frequency calculations e.g `#HF/6-31G(d) OPT FREQ`
- There are many options to this keyword
 - `ReadFC`, `ReadIsotopes`, `Numerical`, `NoRaman`

Normal Modes

- Calculation on water with Gaussian03
- Experimentally observed frequencies are $\nu_1=3657 \text{ cm}^{-1}$, $\nu_2=1595 \text{ cm}^{-1}$, $\nu_3=3756 \text{ cm}^{-1}$
- Experimentally observed intensities are $f_1=3.2 \text{ km mol}^{-1}$, $f_2=64.5 \text{ km mol}^{-1}$, $f_3=46.3 \text{ km mol}^{-1}$
- <http://cmms.chem.pitt.edu/~daniel/h2o-harm.log>

Anharmonicity in polyatomics

- Including anharmonicity is easy for diatomics, but for polyatomics (interesting) things are not so simple.
- Different approaches to finding anharmonic frequencies of polyatomics are
 - Variational (brute-force) approach
 - Vibrational second-order perturbation theory (VPT2 - implemented in Gaussian03)
 - Vibrational self-consistent field (VSCF)
 - Local modes (depending on time)
- We will look (briefly!) at each of these

Variational calculations

- Variational calculations are much more expensive than VPT2 or VSCF calculations.
 - Most calculations on triatomics ($\text{H}_2\text{O}, \text{H}_3^+$)
 - Some calculations on tetra-atomics and even penta-atomics
- Solve vibrational Hamiltonian of the form $\hat{H} = \hat{P} + V$
 - Set up coordinate system (Normal, Internal, Jacobi, Radau)
 - Obtain a potential energy surface. In most cases the accuracy of this surface determines the accuracy of the calculated frequencies
 - Choose basis functions to represent motion in each vibrational coordinate
 - Construct Hamiltonian matrix from the individual matrix elements for various terms of the Hamiltonian $\langle v' | \hat{H} | v \rangle$
 - Diagonalise this matrix ('size-determining step')

Example - H₂O

- Calculation of vibration-rotation spectrum of water from first principles - Polyansky *et al.*, Science, 299, (2003), 539-542
- PES constructed from MRCI/aug-cc-pV6Z calculations at 346 different geometries (each calculation took 2 hours on 64 processors of a SGI Origin 3000 supercomputer)

State	Obs	5Z	6Z	CBS	PS	CBS + CV	Rel	QED	BODC	Nonad
(010)	1,594.74	-2.99	-2.29	-0.32	-2.79	0.48	-0.81	-0.75	-0.32	-0.27
(020)	3,151.63	-4.22	-2.38	-0.78	-5.38	1.16	-1.57	-1.44	-0.56	-0.44
(030)	4,666.78	-6.30	-3.24	-1.52	-7.91	2.05	-2.37	-2.16	-0.78	-0.60
(040)	6,134.01	-9.81	-5.53	-2.74	-10.38	3.20	-3.30	-3.00	-1.06	-0.83
(050)	7,542.43	-14.70	-9.18	-4.71	-12.90	4.82	-4.45	-4.02	-1.41	-1.14
(101)	7,249.81	12.51	10.76	9.32	-4.78	-5.35	1.70	1.43	0.60	2.00
(201)	10,613.35	18.72	16.46	13.97	-6.96	-7.47	2.98	2.57	1.23	-
(301)	13,830.93	25.72	22.81	18.74	-8.41	-8.95	4.59	4.06	2.05	-
(401)	16,898.84	32.56	28.92	23.06	-9.47	-10.17	6.11	5.49	2.74	-
(501)	19,781.10	40.72	35.96	28.68	-9.31	-10.72	9.04	8.28	4.65	-
(601)	22,529.44	51.14	43.41	34.17	-7.61	-11.88	11.69	10.81	5.94	-
(701)	25,120.27	63.29	51.75	38.66	-5.49	-13.13	13.70	12.75	6.46	-
All	σ	22.84	19.74	16.56	10.44	7.85	4.23	3.83	1.90	-

Variational calculations

- Pros
 - Effectively an exact solution of the vibration-rotation problem - so very accurate
 - Can handle all types of vibrations
 - Accuracy of final calculation limited by quality of the calculated potential energy surface
- Cons
 - Very expensive calculations, only applicable to small molecules
 - Difficult to calculate a potential energy surface of very high accuracy

Vibrational SCF

- Vibrational Hamiltonian in mass-weighted normal coordinates

$$\left[-\frac{1}{2} \sum_{j=1}^N \frac{\partial^2}{\partial Q_j^2} + V(Q_1, \dots, Q_N) \right] \Psi_n(Q_1, \dots, Q_N) = E_n \Psi_n(Q_1, \dots, Q_N)$$

- VSCF is based on the Ansatz

$$\Psi_n(Q_1, \dots, Q_N) = \prod_{j=1}^N \psi_j^{(n)}(Q_j)$$

- Application of variational principle leads to

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial Q_j^2} + \overline{V}_j^{(n)}(Q_j) \right] \psi_j^{(n)}(Q_j) = \epsilon_j^{(n)} \psi_j^{(n)}(Q_j)$$

Vibrational SCF

$$\bar{V}_j^{(n)}(Q_j) = \left\langle \prod_{l \neq j}^N \psi_l^{(n)}(Q_l) \middle| V(Q_1, \dots, Q_N) \middle| \prod_{l \neq j}^N \psi_l^{(n)}(Q_l) \right\rangle$$

- In practise, the potential is usually found by assuming only pairwise interactions between normal modes and limiting the expansion to quartic terms

$$V = \sum_{n=ii}^{iv} F_n Q_i^n + F_{ijj} Q_i^2 Q_j + F_{ijj} Q_i Q_j^2 + F_{ijij} Q_i^3 Q_j + \dots$$

Example - H₂O

- Calculation of vibrational spectrum of water in harmonic region - Chaban *et al.*, JCP, 111, (1999), 1823-1829

<i>Ab initio</i> vibrational frequencies, cm ⁻¹					
Excited mode number	MP2/TZP		MP2/aug-cc-pVTZ		Experimental, frequencies, cm ⁻¹
	Harmonic	Correlation-corrected VSCF	Harmonic	Correlation-corrected VSCF	
1	3994	3798	3920	3738	3756
2	3854	3701	3793	3652	3652
3	1615	1548	1638	1561	1595

- For (H₂O)₂ a 16 point grid per coordinate was used → 17088 potential energy evaluations

Vibrational SCF

• Pros

- Included in GAMESS package
- Can be applied to very large systems (thousands of modes)
- Requires an initial Hessian and a number of energy calculations
- Can be improved with VCI, VCC etc (analogous to electronic structure)

• Cons

- Can't handle all types of vibrations (progressions), highly excited states
- Don't always know where to truncate the potential energy surface expansion
- Very dependent on the source of coordinates chosen

Vibrational Perturbation theory

- Implemented in Gaussian03 for all methods with analytical Hessians (HF,DFT,MP2)
- The zeroth order Hamiltonian is the harmonic oscillator (normal mode) Hamiltonian
- Anharmonicity is included as a perturbation

$$\hat{H}_{VPT2} = \hat{H}_{HO} + \hat{H}_{anh}$$

- Vibrational energies found from second-order perturbation theory

Vibrational Perturbation theory

- \hat{H}_{anh} includes force constants that are cubic and quartic

$$\hat{H}_{anh} = \sum_{ijk} F_{ijk} Q_i Q_j Q_k + \sum_{lmno} F_{lmno} Q_l Q_m Q_n Q_o$$

- The derivatives F_{ijk} and F_{lmno} are found by numerical differentiation of the analytical Hessian at geometries slightly displaced from equilibrium
- In Gaussian03, terms of at most three distinct indices are included (i.e. only F_{1233} no F_{1234})
- At most, need Hessian matrices at 6N-11 different points

From Gaussian03

- Calculation on water with Gaussian03
- VPT2 analysis is only available for models with analytical Hessians (Hartree-Fock, DFT, CIS and MP2) requested with `FREQ=ANHARMONIC`
- Experimentally observed frequencies are $\nu_1=3657 \text{ cm}^{-1}$, $\nu_2=1595 \text{ cm}^{-1}$, $\nu_3=3756 \text{ cm}^{-1}$
- <http://cmms.chem.pitt.edu/~daniel/h2o.log>

Example - H₂O

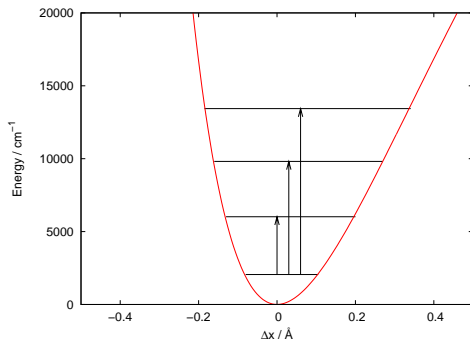
- Calculation of vibrational spectrum of water with VPT2 and the aug-cc-pVTZ basis set - Barone, JCP, 122, (2005), 014108

	BLYP	HCTH	B3LYP	B98	B97-2	PBE0	B1B95	MP2	Expt.
ω_1	3655	3785	3796	3836	3860	3856	3836	3822	3832
ω_2	1596	1620	1627	1634	1645	1633	1628	1628	1648
ω_3	3757	3897	3899	3940	3968	3961	3941	3948	3943
ν_1	3480	3614	3631	3678	3701	3698	3686	3653	3657
ν_2	1543	1571	1575	1583	1594	1582	1578	1578	1595
ν_3	3567	3710	3720	3768	3794	3789	3778	3767	3756
Δ_1	-175	-171	-165	-158	-159	-171	-150	-169	-175
Δ_2	-53	-49	-52	-51	-51	-51	-50	-50	-53
Δ_3	-200	-187	-179	-172	-172	-172	-163	-181	-187

Vibrational Perturbation theory

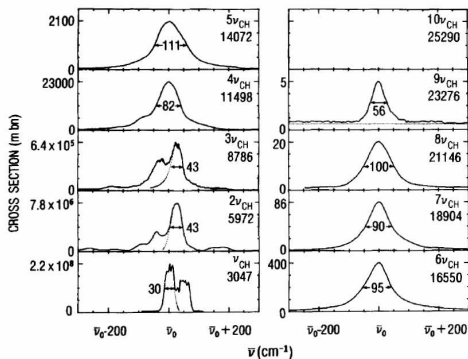
- Pros
 - Easily automated and available in a commercial package
 - Results of reasonable accuracy
- Cons
 - Can't handle all types of vibrations (progressions), highly excited states
 - Potential energy surface truncated at reasonably low order
 - Fairly expensive, requires a large number of Hessian calculations
 - Only applicable to modes where the harmonic term dominates the shape of the potential
 - Have to be careful when dealing with vibrational (Fermi) resonances

Overtone vibrations



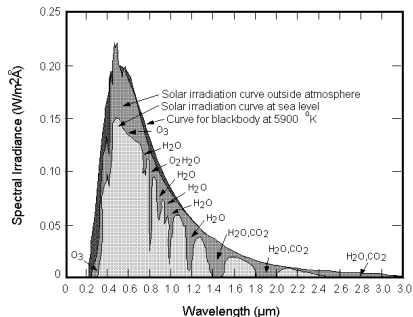
- Both VSCF and VPT2 have difficulty in dealing with highly vibrationally excited modes.

- If we think about benzene (C_6H_6)
 - Have $3N-6=30$ vibrational modes
 - Actual overtone spectrum is very 'clean' (OH-, NH- and CH-stretching modes) \rightarrow local modes



Reddy *et al.* JCP, 76, 2814 (1982)

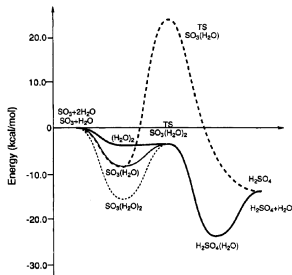
Why are high overtones important?



- Atmospheric absorption
- Vibrational photochemistry

Atmospheric photolysis of sulfuric acid

- Every year at polar sunrise there is a sulfate aerosol bloom over Antarctica
- It was postulated that H_2SO_4 is the source of antarctic SO_2



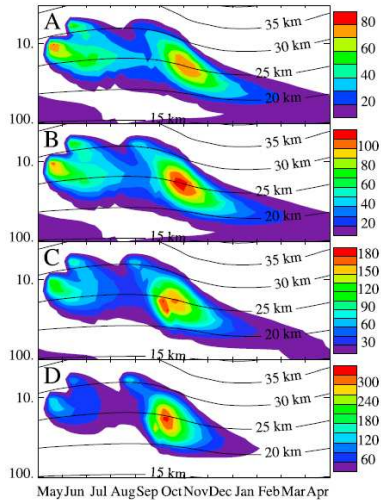
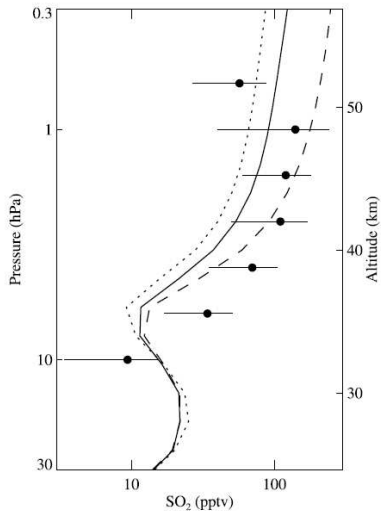
Barrier ~ 35 kcal/mol at MP4SDQ/6-311+G(d,p). Morokuma and Muguruma, JACS, 116, 10316 (1994)

- We might expect $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$ to occur via an electronic transition (high f)
- Ab initio calculations (CIS, MRCI, CC2) show that the lowest lying electronic transition in H_2SO_4 occurs around 140 nm
- It has been shown that dissociation of H_2SO_4 following excitation of an OH-stretching overtone is responsible (Vaida et al. Science, 299, 1566, (2003))
- The barrier to dehydration of sulfuric acid is ~ 35 kcal/mol = ~ 12200 cm^{-1} , which is approx. the energy of the third OH-stretching overtone

- Calculate the first order rate constant for photolysis

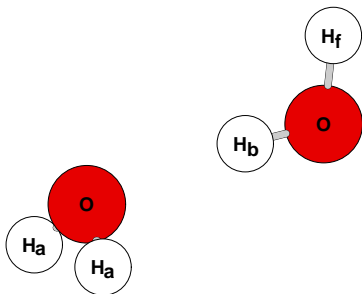
$$J = \int f(\lambda)\phi(\lambda)I(\lambda)d\lambda$$

- Get $f(\lambda)$ from LM calculation
- LM $\tilde{\omega}$ and $\tilde{\omega}_x$ from experiment
- Ab initio calculated dipole moment function \rightarrow evaluate $f \propto \langle e|\vec{\mu}|g\rangle^2$
- Plug into atmospheric model



Water complexes and atmospheric absorption

- $\text{H}_2\text{O}\cdot\text{O}_2$, $\text{H}_2\text{O}\cdot\text{N}_2$, $\text{H}_2\text{O}\cdot\text{H}_2\text{O}$ as atmospheric absorbers



Coupled oscillators

- Instead of beginning with harmonic oscillators/normal mode, we could begin with anharmonic (Morse) local mode oscillators and include coupling as the perturbation
- For two coupled oscillators

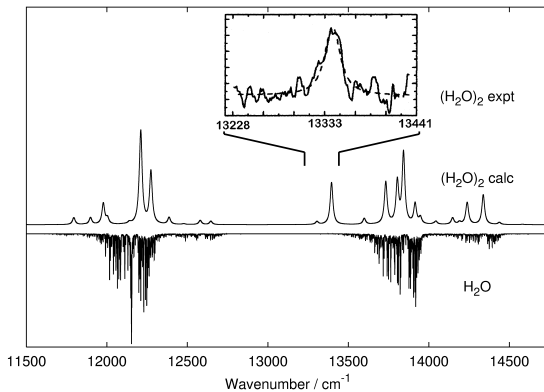
$$\hat{H} = \hat{H}_{Morse} + \hat{H}_{coup}$$

$$\hat{H} = \sum_{i=1}^2 \left(g_{ii} \frac{1}{2} p_i^2 + D_i [1 - e^{-a_i q_i}]^2 \right) + F_{12} q_1 q_2 + g_{12} p_1 p_2$$

- Parameters can be obtained from ab initio calculations

Water complexes and atmospheric absorption

- Calculations on $\text{H}_2\text{O}\cdot\text{H}_2\text{O}$ are a big help for experimentalists



Water complexes and atmospheric absorption

- Our calculations can give an estimate of atmospheric absorption by these complexes

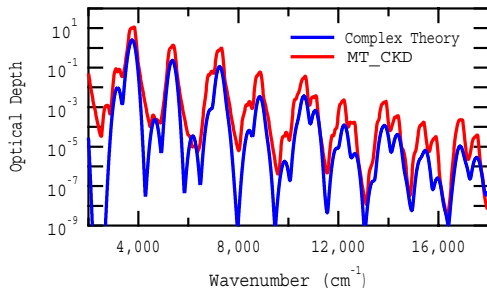


Figure 1

Local mode theory

- Pros
 - Relatively inexpensive
 - Results of reasonable accuracy
 - Can handle all kinds of vibrations
 - Applicable to highly vibrationally excited states
- Cons
 - Of limited accuracy in the fundamental and first overtone regions (coupling terms of low accuracy)
 - Often have to code up vibrational Hamiltonian yourself (difficult to automate)