

# Intermediate Molecular Modeling:

## Spectroscopy



# Spectroscopy

---

## Overview:

- I. Prediction of Vibrational Frequencies (IR)
- II. Prediction of Electronic Transitions (UV-Vis)
- III. NMR Predictions
- IV. Parallel processing (geometry optimization)

# I. Prediction of Vibrational Frequencies

## Purposes:

- IR data helps determine molecular structure and environment
  - Compare experimental vs. computed spectra
    - “Fingerprint” region – assignments difficult
- Computational chemistry programs can *animate* the vibrational modes
  - Useful in an educational setting
    - Students better understand motions involved

# Review

## Normal Modes:

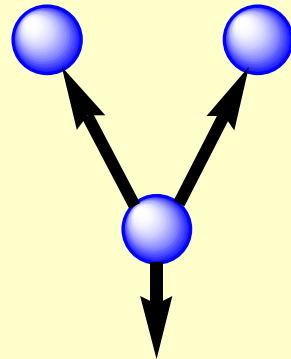
Nonlinear:  $3N-6$  normal modes

Linear:  $3N-5$  “ “

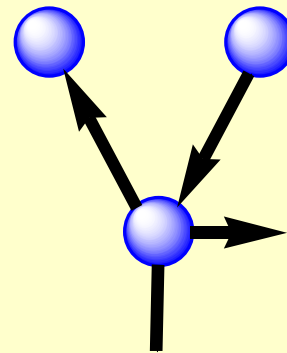
- Bond stretches: Highest in energy
- Bends: Somewhat lower in energy
- Torsional motions: Lower still
- “Breathing” modes (very large molecules):
  - Lowest energy
- Only modes which cause a *change in dipole moment* will be IR active

# Types of Motion - Animations

## Stretching



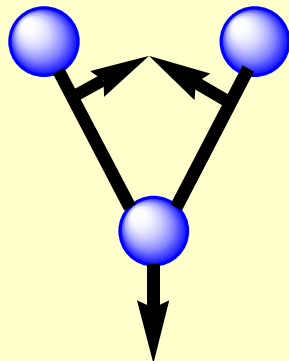
Symmetric



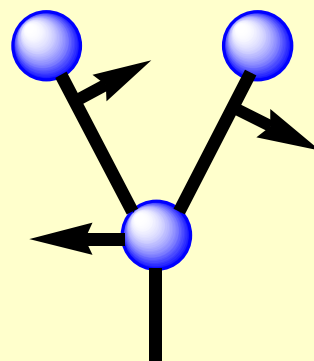
Asymmetric

## Bending

### In Plane

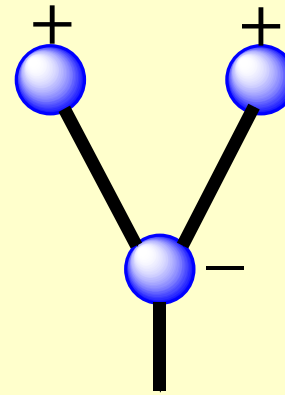


Scissoring

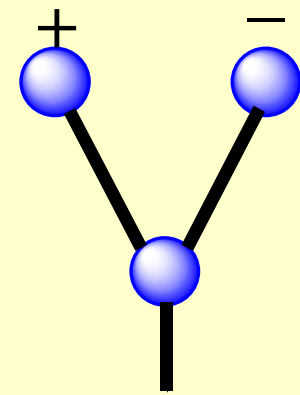


Rocking

### Out of Plane



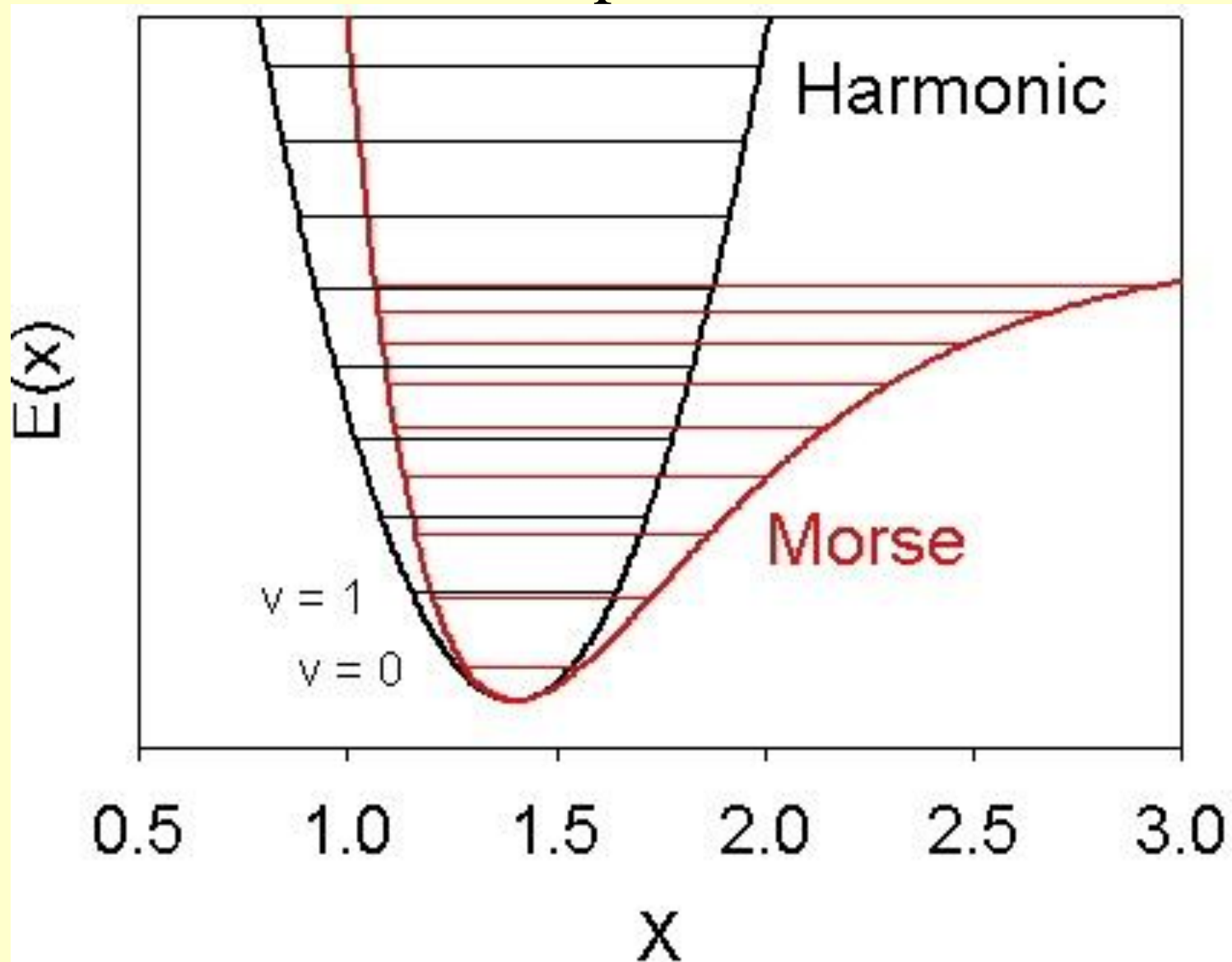
Wagging



Twisting

# Harmonic Oscillator vs. Morse

## Comparison



# Which Model to Use

- Under experimental conditions, vibrational transitions observed are between the ( $v = 0$ )  $\rightarrow$  ( $v = 1$ ) states
  - Both models are nearly the same for this fundamental vibration (See previous slide)
- Since the “real” (Morse) PES is shallower, frequencies calculated in the above manner are always greater than the actual (experimental) frequencies – (more on this later)

# Method Comparison

- **MM** – force fields are empirically created to describe atomic motions
  - Limitation: Many molecules of interest will not have an adequate MM force field available
- **Semiempirical** – Depends on the parameters
  - Molecule of interest vs. training set used
  - In general: **PM3** is better than **AM1**
  - Systematic errors: Multiply frequencies by a scaling (i.e. fudge!) factor

# Method Comparison - continued

- **HF** – Calc. frequencies are  $\sim 10\%$  too high
  - Due to the HOA, and lack of  $e^-$  correlation
  - Much better results can be obtained by scaling the calculated frequencies by a factor of  $\sim 0.9$
- **DFT** – smaller deviations than semiempirical results
  - Overall systematic errors with the better DFT functionals are less than those obtained using Hartree-Fock

# Scaling factors (pg. 340, Cramer, 2<sup>nd</sup> Ed.)

(More extensive list at: <http://srdata.nist.gov/cccbdb/>)

<b>Level of Theory</b>	<b>Scale factor</b>	<b>RMS error (cm<sup>-1</sup>)</b>	<b>Outliers (%)<sup>1</sup></b>
AM1	0.9532	126	15
PM3	0.9761	159	17
HF/3-21G	0.9085	87	9
HF/6-31G(d)	0.8953	50	2
BLYP/6-31G(d)	0.9945	45	2
B3LYP/6-31G(d)	0.9614	34	1
B3PW91/6-31G(d)	0.9573	34	2

1) Number of frequencies still in error by more than 20% of the experimental value after application of the scaling factor

# Exp. vs. Calc. frequencies (cm<sup>-1</sup>) for formamide

All results scaled using factors from previous Slide

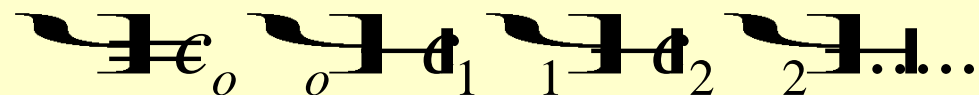
<b>Experimental</b>	<b>PM3</b>	<b>HF/6-31G(d)</b>	<b>B3LYP</b>
3564	3451	3556	3571
3439	3346	3435	3445
2854	2846	2877	2851
1754	1869	1788	1768
1577	1613	1609	1577
1390	1219	1400	1382
1258	1103	1234	1232
1046	1004	1059	1020
1021	916	1038	1005
603	728	603	628
581	482	553	543
289	371	101	92

## II. Prediction of Electronic Transitions

- In order to obtain energies of electronic excited states, the following steps are taken:
  1. A geometry optimization is performed for the ground state molecule
    - Could use MM, Semiempirical, HF, or DFT methods to do this
  2. Ground state wavefunction is calculated, generating occupied and virtual (unoccupied) orbitals
    - Could use Semiempirical, HF, or DFT methods

# Steps - continued

3. Typically, a CIS (Configuration Interaction, Singles) calculation is performed
  - Virtual orbitals ( $\Psi_i$ ) are mixed into the ground state wave-function ( $\Psi_o$ ) (i.e. electrons are swapped between occupied and virtual orbitals obtained from the ground state geometry)
  - The geometry is held constant
  - To keep a small number of excited states, only orbitals near the HOMO and LUMO are used (restricted active space)



$c_i$  = mixing coefficients

## Steps - continued

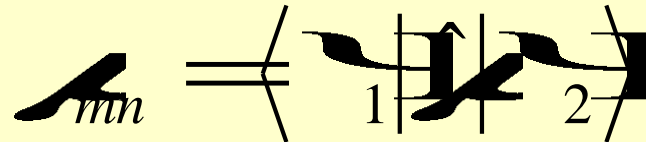
4. Ground state molecular electronic Hamiltonian is used to find the coefficients of mixing
- This gives an approximation to the energy of the excited electronic states *at the fixed molecular geometry* chosen to begin with (i.e. the ground state energy does not change)

5. Transition frequency found by: 
$$\frac{E_{\text{ex}} - E_{\text{g}}}{h}$$

- Note this gives a *vertical excitation energy*, since  $E_{\text{ex}}$  will not be in its equilibrium geometry
- O.K. for short-lived excited states (as in UV-Vis)

# Steps - continued

6. Transition intensity depends on the *energy* and the *oscillator strength*
- Oscillator strength depends on the *transition dipole moment* between any two states (selection rules)

$$A_{mn} = \left| \int \psi_1^* \hat{\mu} \psi_2 \right|^2$$
The diagram shows the mathematical expression for the transition dipole moment squared,  $A_{mn} = \left| \int \psi_1^* \hat{\mu} \psi_2 \right|^2$ . The integrand consists of three parts: a bra state  $\psi_1^*$  on the left, a dipole moment operator  $\hat{\mu}$  in the middle, and a ket state  $\psi_2$  on the right. The wavefunctions are represented by shaded regions with positive and negative lobes. The operator  $\hat{\mu}$  is represented by a vertical arrow pointing upwards. The entire expression is enclosed in large square brackets with a vertical bar on the left, indicating an absolute value.

# Methods

- Ground state geometry
  - MM, Semiempirical, HF, or DFT
- CIS - Semiempirical or *ab initio* methods
  - Time-dependent DFT (TDDFT)
    - Works well for lower energy excitations
    - Ability to do this not included in all programs
- ZINDO – Semiempirical tech. for UV-Vis
  - Theoretical-based calibration
    - Many elements have parameters available
  - “Calibrate” results for species of interest

# Representative Results

- Calc. gas phase (ZINDO CI at MM/PM3 Geometry)

Compound	Exp.(nm)	Calc.(nm)	Assignment
1,3-butadiene	217	213	$\pi \rightarrow \pi^*$
1,3,6-hexatriene	253	253	$\pi \rightarrow \pi^*$
1,3-cyclohexadiene	256	254	$\pi \rightarrow \pi^*$
Napthalene	221, 286, 312	219, 268, 308	$\pi \rightarrow \pi^*$
Acetophenone	240	193	$\pi \rightarrow \pi^*$
	319	272	$n \rightarrow \pi^*$
Benzophenone	252	192	$\pi \rightarrow \pi^*$
	325	270	$n \rightarrow \pi^*$

☼ **Liquid Phase**

# NMR Spectroscopy

- Chemical shift is the most important magnetic property
  - Most widely applied spectroscopic technique for structure determination
  - In addition to  $^1\text{H}$  and  $^{13}\text{C}$ , many other nuclei are increasingly important ( $^{15}\text{N}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ , etc.)
  - All are equally amenable to computational investigation
  - Need to know  $e^-$  density at the nucleus of an atom

# NMR - continued

- Computed magnetic properties are *very sensitive* to the geometry used – **Optimize the geometry first!**
  - An origin must be specified defining the coordinate system for the calculation; The operators used depend on this origin
  - Exact  $\Psi$  gives *origin independent* results
  - $\Psi_{\text{HF}}$  will also give origin independent results *if* a complete basis set is used
    - Since neither of these are likely, the calculated results will depend on the origin used

# Gauge Origin - continued

- Use “Gauge Including Atomic Orbitals”
  - Special basis functions are used
  - Most popular technique, probably the most robust
  - Based on perturbation theory
  - Uses HF or DFT wavefunction to calculate shielding tensors
  - Programs like Gaussian use this method

# NMR Calculations – cont.

- Heavy atom chemical shifts for first row elements can be computed with a fair degree of accuracy
  - In general:  $\text{CCSD(T)} > \text{MP2} > \text{DFT} > \text{HF}$
  - $\text{CCSD(T)}$  &  $\text{MP2}$  usually not feasible due to high computational cost

# NMR Calculations

- $^1\text{H}$ -NMR: DFT method shows best results:
  - 80 modest-size organics: B3LYP rated best
  - Linear scaling improved results (factor = 0.9422)
- $^{13}\text{C}$ -NMR: Larger chemical shift range
  - Large basis sets give the best results
    - Need good values for the  $e^-$  density at the nucleus
  - *Minimum* recommendation
    - B3LYP/6-31G(d) for geometry and NMR calcs.

# Spin-Spin Coupling Calculations

- Less routine than chemical shift calculations
  - Additional complication associated with 2 local magnetic moments
  - Experimentally,  $^1\text{H}/^1\text{H}$  couplings are usually reported
    - These are the *most difficult* to calculate
    - Tend to be small in magnitude, so absolute errors are magnified
  - Best results: Use *very* flexible basis sets
    - Computational expense can be high
  - **Gaussian does do these calculations**

# Hands-On Exercises

- **IR:** Formaldehyde using different methods
  - Compare with experimental results
- **UV-Vis:** Two forms of Phenolphthalein
  - Initial structure will be provided
- **NMR:** Benzene, ethanol, 1-chloroethane
  - Compare  $^1\text{H}$  and  $^{13}\text{C}$  with experimental results
- **Parallel processing:** Benzene geom. opt.
  - Comparison of times using 1,2, or 4 cores