Session 7

Spectroscopy and Thermochemistry

Session 7

Overview:

Part A

I. Prediction of Vibrational Frequencies (IR)

II. Thermochemistry

Part B

III. Prediction of Electronic Transitions (UV-Vis)

IV. NMR Predictions

I. Prediction of Vibrational Frequencies

Purposes:

1. IR data helps determine molecular structure and environment
   - Compare experimental vs. computed spectra
     - “Fingerprint” region – assignments difficult
2. Identifying transition state structures
   - Nature of stationary points on the PES
3. Compute force constants for a geometry optimization

Prediction of Vibrational Frequencies

Purposes:

4. Compute zero point vibration and thermal energy corrections to the total energies, as well as other thermodynamic quantities of interest

Enthalpy (H), Entropy (S), Free energy (G), etc.

Review

Normal Modes:

Nonlinear: 3N-6 normal modes

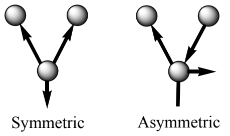
Linear: 3N-5 " "

- 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

---

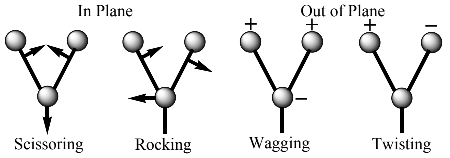
Types of Motion - Animations

Stretching



Symmetric Asymmetric

Bending



Scissoring Rocking Wagging Twisting

Harmonic Oscillator Approximation

- Based on Hooke's Law:

$$\tilde{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\frac{M_a M_b}{M_a + M_b}}\right)^{\frac{1}{2}}$$

$\tilde{\nu}$ = vibrational frequency (cm^{-1})

Atomic masses (g) are M_a and M_b

$c =$ velocity of light (cm / sec)

$k =$ bond force constant (dynes / cm)

A Better Description ?

– When stretched enough, a bond will break

Bond stretching is more accurately described using a *Morse potential:*

$$E_{Morse}(r_{ab}) = D_{ab}\left\{1 - e^{-\alpha_{ab}(r_{ab} - r_0)}\right\}^2$$

D_{ab} = bond dissociation energy

$\alpha = \sqrt{k_{ab} / 2D_{ab}}$ $\quad k_{ab}$ = force constant

r_{ab} = internuclear distance $\quad r_o$ = "equilibrium" bond length

Morse potential: Approximation to an anharmonic oscillator

Differences

– Harmonic Oscillator Approximation gives infinite number of evenly spaced energy levels given by:

$E = h\nu\left(\text{v} + \frac{1}{2}\right)$ $\quad \nu$ = frequency of the vibration

v = vibrational quantum number (0, 1, 2, etc.)

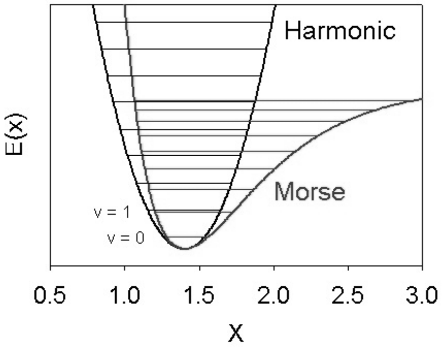
When v = 0, E is the zero-point energy $\left(E_o = \frac{h\nu}{2}\right)$

– Morse Potential

- Vibrational energy levels more closely spaced at higher quantum number (due to anharmonicity) and are finite in number (See next slide)

Harmonic Oscillator vs. Morse

Comparison



Which Model to Use

- Under experimental conditions, vibrational transitions observed are between the (v = 0) → (v = 1) states
  - Both models are nearly the same for this fundamental vibration (See previous slide)
- Computationally: Easier to deal with polynomial expressions (HOA) than with exponential expressions (MP)
  - →HOA is most commonly used for computing molecular vibrational frequencies
  - More accurate methods *could* be used, at the expense of increased CPU time

Calculations

- Normal modes of vibration are centered at the equilibrium geometry of the molecule
  - →Structure *must* be optimized prior to the start of a frequency calculation
  - Frequency calculations are only valid at stationary points on the PES
- Frequency calculations should be computed *at the same level of theory* used to optimize the molecule
  - Frequencies should all be *positive* for an optimized structure (stationary point on PES)
    - If imaginary (negative) frequencies are found, the geometry represents a saddle point on the PES

Calculations - continued

- 2nd derivative of the energy (*E*) w.r.t. the Cartesian nuclear co-ordinates gives the curvature at the bottom of the PES (Slide #9)
- 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
  - Can get usable results using the HOA and if the compound of interest is similar in structure to those used to create the force field
  - Limitation: Many molecules of interest will not have an adequate MM force field available
- Molecular vibrations are therefore best investigated using a quantum mechanical approach

Method Comparison - continued

- **Semiempirical** – Depends on the parameters
  - If the molecule of interest is similar to the training set, qualitative results can be obtained
  - Calculated frequency values are often erratic
  - In general: **PM3** is better than **AM1**
  - To compensate for systematic errors and get better agreement with experimental results, some authors will multiply PM3 and AM1 frequencies by a scaling factor (See Slide #18)

Method Comparison - continued

- **HF** – Calc. frequencies are ~10% too high
  - This is due to: (1) The HOA, and (2) the lack of electron correlation in the calculation
  - These (known) systematic errors can be compensated for
  - Much better results can be obtained by scaling the calculated frequencies by a factor of ~0.9
    - The best scaling factor depends on the basis set used (See Slide #18)
  - 6-31G(d) is the smallest basis set that gives decent results for a variety of molecules

Method Comparison - continued

- **DFT** – Erratic behavior (sometimes), but with smaller deviations than semiempirical results
  - Overall systematic errors with the better DFT functionals are less than those obtained using Hartree-Fock
  - The pure DFT functional BLYP requires little scaling
    - Errors are random about the experimental values
  - Hybrid DFT functionals which include HF character need to be scaled, since they again give consistently high results

Scaling factors (pg. 340, Cramer, 2nd Ed.)

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

Level of Theory	**Scale factor**	**RMS error (cm^{-1})**	**Outliers (%)[1]**
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^{-1}) for formamide

All results scaled using factors from Slide #18

Experimental	PM3	HF/6-31G(d)	B3LYP
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

Peak Intensities

- Intensities can help in peak assignments,

  Can get *relative* intensities using the wavefunction to compute the transition dipole moments

  – *Ab initio*: Preferred way of doing this (semiempirical methods often give poor results)
    - HF results are often scaled
    - Scaled HF, DFT, MP2 all give similar accuracies
    - Hybrid DFT functionals give best results
    - Higher-level correlated methods (CISD, CCSD) give improved values, but the computational cost is high

Vibrational Frequencies: Summary

– Computational methods are a powerful tool to gain insight into molecular vibrational motion

– Different methods will produce different degrees of agreement with experimental results

– Best: Use HF or DFT with a scaling factor

– If HF or DFT can’t be used, try MM or semiempirical methods, but beware of limitations

→If working with new compounds, try to “calibrate” your frequency calculations using similar, known compounds that have experimental data available

II. Thermochemistry

- Once vibrational frequencies are calculated, it takes a small amount of CPU time to compute various thermochemical parameters
  - Results are usually included in program output
- As with IR calculations, a bad starting geometry can give incorrect thermodynamic results
  - Optimize geometry, THEN calculate the vibrational frequencies using the same (or higher) level of theory
- To relate calculated molecular properties to macroscopic thermodynamic properties, *statistical mechanics* is used

Statistical Mechanics

- Quantum mechanics depends on Ψ

  Appropriate operator → Property of interest
- Statistical mechanics depends on the *partition function*, which allows calculation of macroscopic values
  - Partition function (q) for a single molecule is a sum of exponential terms involving all possible quantum energy states (ε_i):

$$q = \sum_{i}^{\text{all states}} e^{-\varepsilon_i / k_B T}$$

Statistical Mechanics - continued

- Partition function (Q) for N identical molecules: $Q = q^N / N!$
- The molecular partition function (q) may also be written as a sum over all distinct energy levels multiplied by a degeneracy factor (g_i):

$$q = \sum_{i}^{\text{all levels}} g_i e^{-\varepsilon_i / k_B T}$$

  - Once the partition function is determined, a number of thermochemical and macroscopic observables can be calculated (Next two slides)

Relationships

Internal energy (*U*): **Helmholtz free energy (*A*):**

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V \qquad A = -k_B T \ln Q$$

Pressure (*P*): $P = -\left(\frac{\partial A}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T$

Constant volume heat capacity (C_v):

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = 2k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_V + k_B T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V$$

Other Relationships

Enthalpy (*H*):

$$H = U + PV = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V + k_B T V \left(\frac{\partial \ln Q}{\partial V}\right)_T$$

Entropy (*S*):

$$S = \frac{U - A}{T} = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_V + k_B \ln Q$$

Gibbs free energy (*G*):

$$G = H - TS = k_B T V \left(\frac{\partial \ln Q}{\partial V}\right)_T - k_B T \ln Q$$

Partition functions

- Molecular energy can be approximated as a sum of the various contributions:

$$\varepsilon_{tot} = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$$

- The partition function then becomes a product of terms: $q_{tot} = q_{trans} q_{rot} q_{vib} q_{elec}$
- Enthalpy and Entropy involve ln(q), so:

$$H_{tot} = H_{trans} + H_{rot} + H_{vib} + H_{elec}$$

$$S_{tot} = S_{trans} + S_{rot} + S_{vib} + S_{elec}$$

Partition Function Contributions

- **Translational:** Only need MW

$$q_{trans} = \left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} V$$

$$M = MW;\; V = \text{ Molar gas volume}$$

- **Rotational:**

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}\sqrt{I_1 I_2 I_3}$$

Where I_i = Moment of inertia; σ = # of distinct proper rotational operations plus the identity operation

Partition Function Contributions

- **Vibrational:**
  - Total molecular vibrational energy = sum of energies for each vibration. Total partition function is a product of partition functions for each vibration

$$q_{vib} = \prod_{i=1}^{3n-6} \frac{\exp\left(-h\nu_i / 2k_B T\right)}{1-\exp\left(-h\nu_i / k_B T\right)}$$

- **Electronic:**
  - Only ground electronic state is considered
    - Excited states typically lie much higher in energy
  - Most molecules have a nondegenerate ground state, which means: $q_{elec} = 1$

Zero Point Energy (ZPE)

- In comparing theoretical energies of individual molecules (calc. at 0K, fixed nuclei) to experimental results (done at ~298K with vibrating nuclei), ***two corrections*** are normally required:

1. Zero-point energy (ε_o): At 0K, a molecule will have vibrational energy. Summation of energy over all vibrational modes gives:

$$\varepsilon_0 = H_{vib}(0) = \frac{1}{2} h \sum_{\text{i}}^{\text{normal modes}} \nu_{\text{i}}$$

→ **May** need to add zero-point energy to total energy

Thermal Energy

2. At temperature (T) above 0K, ΔH is given by:

$$\Delta H(T) = U_{trans}(T) + U_{rot}(T) + \Delta U_{vib}(T) + RT$$

$$U_{trans}(T) = \frac{3}{2}RT \quad \mathrm{U}_{\mathrm{rot}}(T) = \frac{3}{2}RT \quad (= RT \text{ if linear})$$

$$\Delta U_{vib}(T) = U_{vib}(T) - U_{vib}(0) = Nh \sum_{\mathrm{i}}^{\substack{\text{normal}\\ \text{modes}}} \frac{\nu_i}{e^{h\nu_i / k_B T} - 1}$$

- This calculation takes into account the effects of molecular translation, rotation, and vibration at the temperature of interest
- Note that the thermal energy correction *includes the ZPE automatically*

Scaling Factors

– As with frequencies, ZPE and thermal energy values are scaled to eliminate systematic errors.

– Same value used for frequencies may be used, or specific factors for energies may be used

Level of Theory	**Frequency Scale factor**	**ZPE/Thermal energy scale factor**
HF/3-21G	0.9085	0.9409
HF/6-31G(d)	0.8929	0.9135
BLYP/6-31G(d)	0.9940	1.0119
B3LYP/6-31G(d)	0.9613	0.9804

Adapted from Foresman & Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd. Ed., p. 64

Program Output - Semiempirical

Output varies by program and by method used

MOPAC (CAChe) default values listed in ***mopac.out*****:**

$\Delta_f H°$, I_i, MW, Point group, ZPE, enthalpy, C_p, and entropy at variety of temperatures. Includes individual partition function values for vibration, rotation, and translation

(1) **Electronic energy** = Sum of potential energies for all electrons in the molecule (negative number)

(2) **Core-Core repulsion energy** = Nuclear repulsion

(3) **Total energy** (not printed) = (1) + (2)

(4) **Atomization energy** = $-(3) + \sum_{i}^{N} E_{\text{atomization, exp}}(i)$

(5) **Heat of Formation** = $\Delta_f H = \sum_{i}^{N} \Delta_{f,\exp} H(i) - (4)$

Program Output – *DFT*

DGauss (CAChe) default values listed in *DGauss.log*:

- Quantities from IR frequency calculations
- ZPE, total energy, and the rotational symmetry number (σ), heat capacity, enthalpy, entropy, and free energy values at a variety of temperatures

(1) **Energy** (a.u.) = electronic energy + core-core repulsion energy

(2) **Zero point energy** (positive number)

(3) **Total energy** = (1) + (2)

- The total energy is not converted into $\Delta_f H$, as the errors would be large
- Total energies can be compared to calculate reaction energies, relative stabilities of isomers, etc.

Representative Results

- Calc. of $\Delta_r H^o$ for:

$$CO_2 + CH_4 \rightarrow 2\ H_2CO$$

(Exp. Value: 59.9 ± 0.2 kcal/mole)

Method	Result (kcal/mole)
AM1	25.7
PM3	29.9
PM5	41.6
B88-LYP	58.4

Session 7: Part B

III. Prediction of Electronic Transitions (UV-Vis)

IV. NMR Predictions

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 (Ψ_i) are mixed into the ground state wave-function (Ψ_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)

$$\Psi = c_o\Psi_o + c_1\Psi_1 + c_2\Psi_2 + ...$$

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: $\nu = \dfrac{E_{\text{ex}} - E_{\text{g}}}{h}$
   – Note this gives a *vertical excitation energy*, since E_{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)

$$\boldsymbol{\mu}_{mn} = \left\langle \Psi_1 \middle| \hat{\boldsymbol{\mu}} \middle| \Psi_2 \right\rangle$$

Methods

- Ground state geometry
  - MM, Semiempirical, HF, or DFT
- CIS
  - Use semiempirical or *ab initio* methods for this
  - Can use Time-dependent DFT (TDDFT)
    - Works well for lower energy excitations
    - Ability to do this not included in all programs

UV-Vis using ZINDO

- INDO/S (also called ZINDO/S, part of ZINDO)
  - Semiempirical method specifically parameterized to reproduce UV-Vis spectra
    - Other MOPAC methods parameterized for ground-state heats of formation (better suited for geometry optimizations)
  - ZINDO output is in atomic units

ZINDO

- **Z**erner’s **I**ntermediate **N**eglect of **D**ifferential **O**verlap
  - Only uses valence electrons
  - Parameterization is theoretically-based, and more elements have parameters than in MOPAC
  - Can use *d*-orbitals with many transition metals (this is very limited in MOPAC)
  - Used to calculate electronic spectra

ZINDO - continued

- **Limitations of ZINDO:**
  - Handles molecules up to ~200 atoms
  - Strain energy of small ring systems not handled well
  - May have to “calibrate” for particular systems of interest
    - If studying new compounds, do calculations on known compounds of similar structure whose electronic spectra have been measured
    - See how well the calculated spectra match

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	$\pi \rightarrow \pi^*$
☼ **Liquid Phase**	325	270	$n \rightarrow \pi^*$

NMR Spectroscopy

- Chemical shift is the most important magnetic property
  - Most widely applied spectroscopic technique for structure determination
  - In addition to ^{1}H and ^{13}C, many other nuclei are increasingly important (^{15}N, ^{29}Si, ^{31}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!**
- Complex problem
  - More difficult to model the interaction of a wavefunction with a magnetic field (**B**) than an electric field (**E**)
- Electric field (**E**) perturbs the *potential* energy term of the Hamiltonian

NMR Calculation Problems

- Magnetic field (**B**) perturbs the *kinetic* energy term
  - Electron motion produces electronic magnetic moments
  - Angular momentum operator (**L**) is imaginary
  - An origin must be specified defining the coordinate system for the calculation; The operators used depend on this origin
  - Use of the exact Ψ gives *origin independent* results
  - Ψ_{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

- The origin of the coordinate system used for the calculation is called the *gauge origin*
  - One way to eliminate the gauge dependence is to construct basis functions that are dependent on a magnetic field
    - Include a complex phase factor that refers to the position of the basis function (the nucleus)
    - Makes all calculated properties independent of the gauge origin
    - Older versions of this approach called “Gauge Invariant Atomic Orbitals” **(GIAO)**

Gauge Origin - continued

- More recent versions keep the same acronym, that now stands for “**G**auge **I**ncluding **A**tomic **O**rbitals”
  - 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

- There are two magnetic fields to worry about:

$$\text{NMR Chemical Shift } \alpha \left(\frac{\partial^2 E}{\partial B \partial I} \right)$$

B = External magnetic field

I = Nuclear magnetic moment

  - Computing absolute chemical shifts is difficult
    - Shifts are therefore calculated relative to a standard (TMS for ^{1}H and ^{13}C)
    - *Gas phase* results, often reasonably close to experimental

NMR Calculations – cont.

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

---

^{1}H NMR Calculations

- Small chemical shift range (~15ppm)
- Rovibrational and solvent effects give errors comparable to the range of chemical shifts
- DFT method shows best results:
  - 80 modest-size organics: B3LYP rated best
  - GIAO scheme used with a 6-311++G(2df,p) basis set
  - Linear scaling improved results (factor = 0.9422)

---

^{13}C NMR Calculations

- Calculations much more common than for ^{1}H
  - Much larger chemical shift range
  - Large basis sets give the best results
    - It is largely the ‘tails” of the valence orbitals at the nucleus that affect chemical shifts, not the core orbitals
  - *Minimum* recommended combination:
    - B3LYP/6-31G(d) geometry followed by HF/6-31G(d) calc. of the chemical shifts

Spin-Spin Coupling Calculations

- Less routine than chemical shift calculations
  - Additional complication associated with 2 local magnetic moments
  - Experimentally, $^1H/^1H$ couplings are usually reported
    - These are the **most difficult** to calculate
    - Tend to be small in magnitude, so absolute errors are magnified
  - Have to use *very* flexible basis sets, making the cost quite high
  - **Gaussian does do these calculations**

The End

© 2003 United Feature Syndicate, Inc.

- Questions?