Molecular Vibrations

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Why Estimate Molecular Vibrations?

- Simulation of vibrational spectrum (identification of molecules)

- Vibrational corrections to enthalpy

- (Small) vibrational corrections to polarizability and other properties

- Understanding of vibrational motion could assist dynamics experiments and "mode-selective" chemistry

Small Vibrations in Classical Mechanics

The classic reference is Wilson, Decius, and Cross, *Molecular Vibrations* (Dover, New York, 1980). Cheap book, makes a good reference.

Let us focus on purely classical systems at first; all the results carry over to quantum mechanics.

For small vibrations, the motion of atom α away from its equilibrium value may be described by $\Delta x_\alpha, \Delta y_\alpha, \Delta z_\alpha$, with kinetic energy

$$T = \frac{1}{2} \sum_{\alpha=1}^{N} M_\alpha \left[\left(\frac{d\Delta x_\alpha}{dt} \right)^2 + \left(\frac{d\Delta y_\alpha}{dt} \right)^2 + \left(\frac{d\Delta z_\alpha}{dt} \right)^2 \right]$$

If we switch to mass-weighted coordinates, such as $q_1 = \sqrt{M_1}\Delta x_1$, $q_2 = \sqrt{M_1}\Delta y_1$, $q_3 = \sqrt{M_1}\Delta z_1$, $q_4 = \sqrt{M_2}\Delta x_2$, etc., then the kinetic energy operator becomes simpler since the mass factors are now absorbed

$$
\begin{aligned}
T &= \frac{1}{2}\sum_{i=1}^{3N}\dot{q}_i^2 \\
V &= V_0 + \sum_{i=1}^{3N}\left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \cdots
\end{aligned}
$$

$$(1)$$

Remember that at equilibrium, $(\partial V/\partial q_i)_0 = 0$; we can also set $V_0 = 0$. Also abbreviate $(\partial^2 V/\partial q_i \partial q_j)_0$ as just f_{ij}.

Newton's Equations of Motion

We can rewrite Newton's equations of motion as

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}_j} + \frac{\partial V}{\partial q_j} = 0 \quad j = 1, 2, \cdots, 3N$$

or

$$\ddot{q}_j + \sum_{i=1}^{3N} f_{ij} q_i = 0$$

A possible solution to this equation is

$$q_i = a_i cos\left(\sqrt{\lambda}t + \phi\right)$$

where the angular frequency is $\sqrt{\lambda}$; this is just $\sqrt{k/m}$ in harmonic oscillator — the m has been absorbed by the mass-weighted coordinate system used here!

Substitute the last expression into the differential equations to get

$$\sum_{i=1}^{3N} \left(f_{ij} - \delta_{ij}\lambda\right) a_i = 0 \quad j = 1, 2, \cdots, 3N$$

or in matrix notation, just $\underline{\underline{\mathbf{F}}}\,\underline{\mathbf{a}} = \lambda\,\underline{\mathbf{a}}$. *This is an eigenvalue equation!* We have a solution to this system of $3N$ linear equations only if λ has special values obtainable from the secular determinant

$$\begin{vmatrix} f_{11} - \lambda & f_{12} & f_{13} & \cdots & f_{1,3N} \\ f_{21} & f_{22} - \lambda & f_{23} & \cdots & f_{2,3N} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ f_{3N,1} & f_{3N,2} & f_{3N,3} & \cdots & f_{3N,3N} - \lambda \end{vmatrix} = 0$$

Normal Modes of Vibration

The matrix eigenvalue equation is equivalent to matrix diagonalization which is equivalent to solving the secular determinant for each λ (N of them). Once we have the eigenvalues λ_k we can get the corresponding eigenvectors $\underline{\mathbf{a}}_k$, giving the motion of each atom for the given eigenvalue λ_k:

$$q_{ik} = a_{ik} cos\left(\sqrt{\lambda_k}t + \phi_k\right).$$

The eigenvectors $\underline{\mathbf{a}}_k$ are the *normal modes* of vibration. *For each normal mode, all the atoms move with the same frequency and phase, but with different amplitudes.*

Normal Coordinates

We can define a new set of coordinates using the normal modes. This gives us the "normal coordinates"
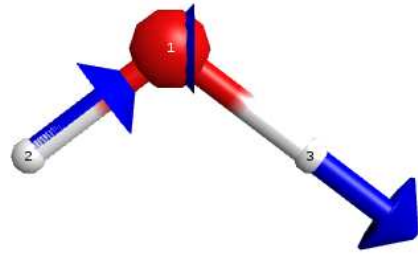
$$Q_k = \sum_{i=1}^{3N} a_{ik} q_i \quad k = 1, 2, \cdots, 3N$$

Since the eigenvectors of a real, symmetric matrix ($\underline{\underline{\mathbf{F}}}$) are orthogonal, T and V become diagonal (no cross terms):

$$T = \frac{1}{2} \sum_{k=1}^{3N} \dot{Q}_k^2$$

$$V = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2$$

The Hamiltonian is separable in this representation!
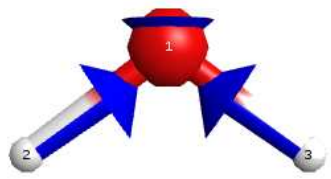
Polyatomic Molecules

What happens for quantum mechanics, and for polyatomic molecules? Use Harmonic Oscillator model.

- $3N$-6 frequencies ($3N$-5 for linear molecules); the rest are translations and rotations with zero frequency

- In normal mode coordinates, Hamiltonian is separable: wavefunction is a product and energy is a sum. Total vibrational energy is $\sum_i \omega_i \hbar (v_i + 1/2)$

- Minimum energy (due to uncertainty principle) is "zero point vibrational energy" (ZPVE or ZPE), where $v_i = 0$ for all i. ZPVE $= \frac{1}{2}\hbar \sum_i \omega_i$

How Would We Get Harmonic Frequencies for a Molecule?

- Easy — just diagonalize the second derivative matrix $\underline{\underline{\mathbf{F}}}$, called the *Hessian*. The frequencies ω_i are the square roots of the eigenvalues, $\sqrt{\lambda_i}$.

- Where do we get $\underline{\underline{\mathbf{F}}}$?

- Recall $f_{ij} = (\partial^2 V / \partial q_i \partial q_j)$

- Potential energy V is just E_e (B.O. approximation!): Need $\partial E_e^2 / \partial q_i \partial q_j$.

- Compute second derivative of E_e in terms of of Cartesian displacements (x_α, y_α, z_α, call them $\tilde{q}_i$) and it's easy to transform to mass-weighted coordinates, using

$$\underline{\underline{\mathbf{F}}} = \underline{\underline{\mathbf{M}}}^{-1/2} \; \underline{\underline{\tilde{\mathbf{F}}}} \; \underline{\underline{\mathbf{M}}}^{-1/2}.$$

- How do we get $\partial^2 E_e / \partial x_\alpha \partial y_\beta$, etc? Need second derivative of electronic energy vs nuclear coordinates. Can compute *analytically* (using formula) or *numerically* from finite differences of energies or gradients:

$$\frac{\partial^2 E_e}{\partial x_\alpha \partial y_\beta} \approx \left[\left(\frac{\partial E_e}{\partial y_\beta} \right) \bigg|_{x_\alpha = x_{\alpha 0} + \Delta x_\alpha} - \left(\frac{\partial E_e}{\partial y_\beta} \right) \bigg|_{x_\alpha = x_{\alpha 0} - \Delta x_\alpha} \right] / \Delta x_\alpha.$$

Analytic Hessian Better than Numerical

- Analytic Hessian might cost $\sim$ 10-30x cost of energy; analytic gradient costs maybe $\sim$ 1.5-2x.

- Can need gradients from many displaced geometries — up to $6N$ (+ and - for each of $3N$ coordinates) — unless reduced by point group symmetry

- Numerical Hessian contains numerical errors (divide small number by small number)

- (Can land on wrong solution if displacement drops symmetry)

Availability of Analytic Derivatives

Method	Gradient	Hessian
HF, DFT	Y	Y
CI	Y	N
CCSD, CCSD(T)	Y	S
MP2	Y	S
CASSCF	Y	S
CIS	Y	Y
EOM-CCSD	S	N
TD-DFT	S	N

S = available in some packages; Y = widely available

Approximate Average Errors in Harmonic Frequencies

(Using polarized double and triple zeta basis sets)

Method	Error
HF	11%
CISD	4-6%
CCSD	1-4%
CCSD(T)	1-3%

Anharmonicity accounts for another $\sim$ 2-3% difference from experimental fundamental frequencies. Many workers employ *scaling factors* for each level of theory to better predict fundamental frequencies.

Spectra of SiC2H2 isomers: DZP CCSD(T)
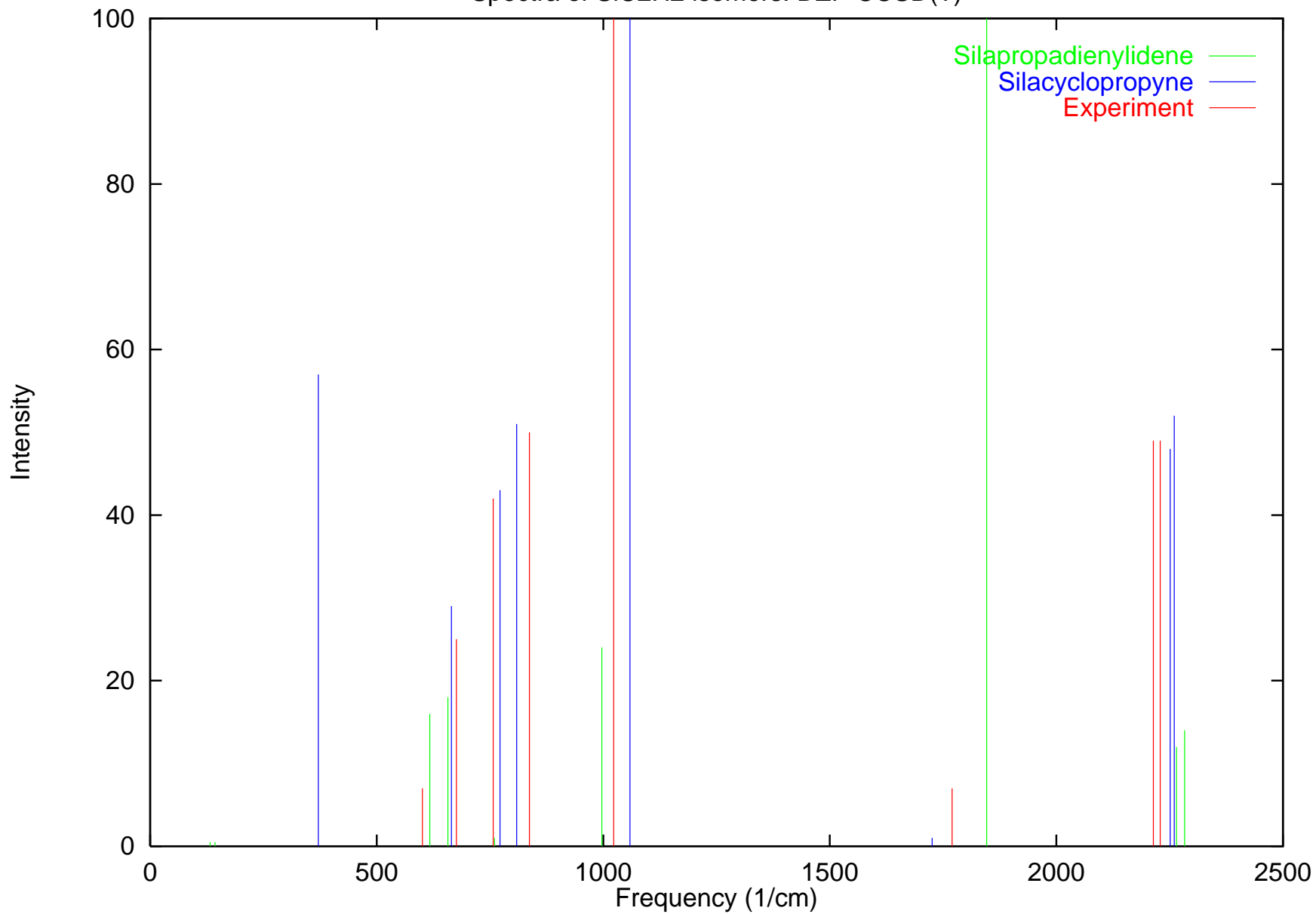
Scaling ZPVE's

In an enlightening paper, Grev, Janssen, and Schaefer [*J. Chem. Phys.* **95**, 5128 (1991)] showed that using scaled fundamental frequencies to estimate the ZPVE is *not* necessarily better than using unscaled frequencies. The reason is anharmonicity.

If ZPVE's use scaling, they should have a *different* scaling factor than the individual frequencies.

$$
G(v) = \sum_r \omega_r \left(v_r + \frac{1}{2} \right) + \sum_{r \geq s} \chi_{rs} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) + \cdots,
$$

$$
\Delta^{harm} = G(0) - ZPVE^{harm} = \frac{1}{4} \sum_r \chi_{rr} + \frac{1}{4} \sum_{r>s} \chi_{rs}.
$$

$$
\Delta^{fund} = G(0) - ZPVE^{fund} = -\frac{3}{4} \sum_r \chi_{rr} - \frac{1}{4} \sum_{r>s} \chi_{rs}.
$$

Characterization of Stationary Points

- A *stationary point* is a geometry $\tilde{\mathbf{q}}$ for which the gradient $\partial E_e(\tilde{\mathbf{q}})/\partial \tilde{q}_i$ for all coordinates $\tilde{q}_i$: can be a (global or local) PES minimum, transition state, or higher order saddle point

- The *Hessian Index* is the number of negative force constants (corresponding to imaginary vibrational frequencies, often printed as negative frequencies)

- For a minimum, verify that there are no imaginary frequencies

- For a transition state, verify there is exactly one unique imaginary frequency

```
*****************************************************************
Running Q-Chem

cicero.chemistry.gatech.edu on Fri Dec 15 14:51:29 EST 2000.

Version: /usr/local/qchem.6.3.00/bin/qchem
         /usr/local/qchem.6.3.00/exe/progman.exe

*****************************************************************
             Welcome to Q-Chem
      A Quantum Leap Into The Future Of Chemistry

 J. Kong, C. A. White, A. I. Krylov, C. D. Sherrill,
 R. D. Adamson, T. R. Furlani, M. S. Lee, A. M. Lee,
 S. R. Gwaltney, T. R. Adams, H. Dachsel, W. M. Zhang,
 P. P. Korambath, C. Ochsenfeld, A. T. B. Gilbert,
 G. S. Kedziora, D. R. Maurice, N. Nair, Y. Shao,
 N. A. Besley, P. E. Maslen, J. P. Dombroski, J. Baker,
 E. F. C. Byrd, T. Van Voorhis, M. Oumi, S. Hirata,
 C. P. Hsu, N. Ishikawa, J. Florian, A. Warshel,
 B. G. Johnson, P. M. W. Gill, M. Head-Gordon, J. A. Pople,
 Q-Chem, Version 2.0, Q-Chem, Inc., Export, PA (2000).


  Intel x86 Linux Version


=======================================================================
User input:
=======================================================================
$comment
Water
$end

$molecule
0 1
O
H1 O OH
H2 O OH H1 HOH

OH  = 0.989276
HOH = 100.0198
$end

$rem
JOBTYPE          FREQ
EXCHANGE         HF
CORRELATION      NONE
BASIS            STO-3G
SCF_FINAL_PRINT  2         Energies plus MOS
$end

=======================================================================
Processing $rem in the input.

####################################################
#  Entering fldman.exe on Fri Dec 15 14:51:30 2000  #
####################################################

    -------------------------------------------------
       Standard Nuclear Orientation (Angstroms)
     I   Atom        X           Y           Z
    -------------------------------------------------
       1    O       0.000000    0.000000    0.127153
       2    H      -0.757939    0.000000   -0.508611
       3    H       0.757939    0.000000   -0.508611
    -------------------------------------------------
 Molecular Point Group                 C2v   NOp =  4
 Largest Abelian Subgroup              C2v   NOp =  4
 Nuclear Repulsion Energy =      8.9077080996 hartrees
```

```
There are        5 alpha and       5 beta electrons
Requested basis set is STO-3G
There are 4 shells and 7 basis functions
A cutoff of  1.0D-10 yielded      10 shell pairs
There are     34 function pairs

####################################################
#  Entering gesman.exe on Fri Dec 15 14:51:30 2000  #
####################################################

Smallest overlap matrix eigenvalue = 3.63E-01
Multipole matrices computed through 2nd order
Guess from superposition of atomic densities
Warning:  Energy on first SCF cycle will be non-variational

####################################################
#  Entering scfman.exe on Fri Dec 15 14:51:30 2000  #
####################################################

A restricted Hartree-Fock SCF calculation will be
performed using Pulay DIIS extrapolation
SCF converges when DIIS error is below 1.0E-08
-------------------------------------------------------
 Cycle       Energy         DIIS Error
-------------------------------------------------------
    1    -74.6061773729     4.01E-01  000000
    2    -74.9233301871     6.78E-02  000000
    3    -74.9653425178     8.77E-03  000000
    4    -74.9658786194     1.57E-03  000000
    5    -74.9659011332     2.76E-05  000000
    6    -74.9659011457     1.08E-05  000000
    7    -74.9659011480     7.89E-08  000000
    8    -74.9659011480     2.72E-08  000000
    9    -74.9659011480     1.03E-08  000000
   10    -74.9659011480     3.60E-10  000000  Convergence criterion met
-------------------------------------------------------
SCF time:  CPU 0.08 s  wall 0.00 s

Final Alpha MO Eigenvalues
               1          2          3          4          5          6
  1 -20.2515674  -1.2576205  -0.5939092  -0.4597630  -0.3926280   0.5819312
               7
  1   0.6928062
Final Alpha MO Coefficients
               1          2          3          4          5          6
  1   0.9942161  -0.2337592   0.0000000  -0.1040490   0.0000000   0.1258359
  2   0.0258496   0.8443968  -0.0000000   0.5382402  -0.0000000  -0.8203442
  3   0.0000000   0.0000000   0.6127098   0.0000000  -0.0000000  -0.0000000
  4  -0.0000000   0.0000000   0.0000000   0.0000000   1.0000000  -0.0000000
  5  -0.0041658  -0.1228911  -0.0000000   0.7558818  -0.0000000   0.7635987
  6  -0.0055852   0.1556051  -0.4492190  -0.2950597   0.0000000   0.7692443
  7  -0.0055852   0.1556051   0.4492190  -0.2950597   0.0000000   0.7692443
               7
  1  -0.0000000
  2   0.0000000
  3   0.9598513
  4  -0.0000000
  5  -0.0000000
  6   0.8147663
  7  -0.8147663
Final Alpha density matrix.
               1          2          3          4          5          6
  1   1.0539352  -0.2276888   0.0000000  -0.0000000  -0.0540635  -0.0112263
  2  -0.2276888   1.0033767  -0.0000000   0.0000000   0.3029695  -0.0275650
  3   0.0000000  -0.0000000   0.3754133  -0.0000000  -0.0000000  -0.2752409
  4  -0.0000000   0.0000000  -0.0000000   1.0000000  -0.0000000  -0.0000000
  5  -0.0540635   0.3029695  -0.0000000  -0.0000000   0.5864768  -0.2421295
  6  -0.0112263  -0.0275650  -0.2752409  -0.0000000  -0.2421295   0.3131021
  7  -0.0112263  -0.0275650   0.2752409  -0.0000000  -0.2421295  -0.0904933
               7
```

```
   1  -0.0112263
   2  -0.0275650
   3   0.2752409
   4  -0.0000000
   5  -0.2421295
   6  -0.0904933
   7   0.3131021
```

```
####################################################
#  Entering anlman.exe on Fri Dec 15 14:51:30 2000  #
####################################################
```

Analysis of SCF Wavefunction

```
-----------------------------------------------------------------
              Orbital Energies (a.u.) and Symmetries
-----------------------------------------------------------------
```

Alpha MOs, Restricted
-- Occupied --
```
-20.252  -1.258  -0.594  -0.460  -0.393
  1 A1    2 A1    1 B1    3 A1    1 B2
```
-- Virtual --
```
  0.582   0.693
  4 A1    2 B1
```

Beta MOs, Restricted
-- Occupied --
```
-20.252  -1.258  -0.594  -0.460  -0.393
  1 A1    2 A1    1 B1    3 A1    1 B2
```
-- Virtual --
```
  0.582   0.693
  4 A1    2 B1
-----------------------------------------------------------------
```

```
              Mulliken Net Atomic Charges

     Atom                Charge (a.u.)
   ------------------------------------
      1 O                  -0.330636
      2 H                   0.165318
      3 H                   0.165318
   ------------------------------------
   Sum of atomic charges =    0.000000
```

```
-----------------------------------------------------------------
                 Cartesian Multipole Moments
-----------------------------------------------------------------
   Charge (ESU x 10^10)
           0.0000
   Dipole Moment (Debye)
       X      0.0000    Y      0.0000    Z     -1.7094
      Tot     1.7094
   Quadrupole Moments (Debye-Ang)
      XX     -4.4859    XY     0.0000    YY     -6.1256
      XZ      0.0000    YZ     0.0000    ZZ     -5.3331
   Octapole Moments (Debye-Ang^2)
      XXX     0.0000   XXY     0.0000   XYY     0.0000
      YYY     0.0000   XXZ    -0.5313   XYZ     0.0000
      YYZ     0.0191   XZZ     0.0000   YZZ     0.0000
      ZZZ    -0.1747
   Hexadecapole Moments (Debye-Ang^3)
      XXXX   -6.7321   XXXY    0.0000   XXYY   -1.8081
      XYYY    0.0000   YYYY   -3.2652   XXXZ    0.0000
      XXYZ    0.0000   XYYZ    0.0000   YYYZ    0.0000
      XXZZ   -1.7388   XYZZ    0.0000   YYZZ   -1.4596
      XZZZ    0.0000   YZZZ    0.0000   ZZZZ   -5.2191
-----------------------------------------------------------------
```

```
####################################################
```

```
#  Entering drvman.exe on Fri Dec 15 14:51:30 2000  #
####################################################
```

```
Calculating MO derivatives via CPHF
   1     10       2    0.009892    0.007094
   2     12       0    0.000000    0.000000    Roots Converged
Calculating analytic Hessian of the SCF energy
Polarizability Matrix (a.u.)
            1          2          3
   1  -5.5054487  -0.0000000  -0.0000000
   2  -0.0000000  -0.0400454  -0.0000000
   3  -0.0000000  -0.0000000  -2.5654448
```

Direct stationary perturbation theory relativistic correction:

```
rels  =       0.031221304489
relv  =      -0.096844180832
rel2e =       0.023322614724
E_rel =      -0.042300261619
```

```
Hessian of the SCF Energy
            1          2          3          4          5          6
   1   0.8044023   0.0000000  -0.0000000  -0.4022012  -0.0000000  -0.3374251
   2   0.0000000  -0.0001352   0.0000000  -0.0000000   0.0000676  -0.0000000
   3  -0.0000000   0.0000000   0.6352335  -0.2165519  -0.0000000  -0.3176168
   4  -0.4022012  -0.0000000  -0.2165519   0.4391751   0.0000000   0.2769885
   5  -0.0000000   0.0000676  -0.0000000   0.0000000  -0.0000838   0.0000000
   6  -0.3374251  -0.0000000  -0.3176168   0.2769885   0.0000000   0.3002754
   7  -0.4022012  -0.0000000   0.2165519  -0.0369740  -0.0000000   0.0604366
   8   0.0000000   0.0000676  -0.0000000  -0.0000000   0.0000162   0.0000000
   9   0.3374251  -0.0000000  -0.3176168  -0.0604366  -0.0000000   0.0173414
            7          8          9
   1  -0.4022012   0.0000000   0.3374251
   2  -0.0000000   0.0000676  -0.0000000
   3   0.2165519  -0.0000000  -0.3176168
   4  -0.0369740  -0.0000000  -0.0604366
   5  -0.0000000   0.0000162  -0.0000000
   6   0.0604366   0.0000000   0.0173414
   7   0.4391751   0.0000000  -0.2769885
   8   0.0000000  -0.0000838   0.0000000
   9  -0.2769885   0.0000000   0.3002754
Gradient time:  CPU 0.59 s  wall 1.00 s
```

```
####################################################
#  Entering vibman.exe on Fri Dec 15 14:51:31 2000  #
####################################################
```

```
**********************************************************************
**                                                                  **
**                    VIBRATIONAL ANALYSIS                          **
**                    --------------------                          **
**                                                                  **
**      VIBRATIONAL FREQUENCIES (CM**-1) AND NORMAL MODES           **
**               INFRARED INTENSITIES (KM/MOL)                      **
**                                                                  **
**********************************************************************
```

```
Frequency:      2169.95                4141.60                4392.63
IR Active:        YES                    YES                    YES
IR Intens:       7.245                 44.303                 29.972
Raman Active:     YES                    YES                    YES
               X      Y      Z      X      Y      Z      X      Y      Z
O          0.000  0.000 -0.069  0.000  0.000  0.052 -0.068  0.000  0.000
H         -0.448  0.000  0.545 -0.570  0.000 -0.416  0.540  0.000  0.453
H          0.448  0.000  0.545  0.570  0.000 -0.416  0.540  0.000 -0.453
```

STANDARD THERMODYNAMIC QUANTITIES AT   298.18 K AND   1.00 ATM

  This Molecule has 0 Imaginary Frequencies