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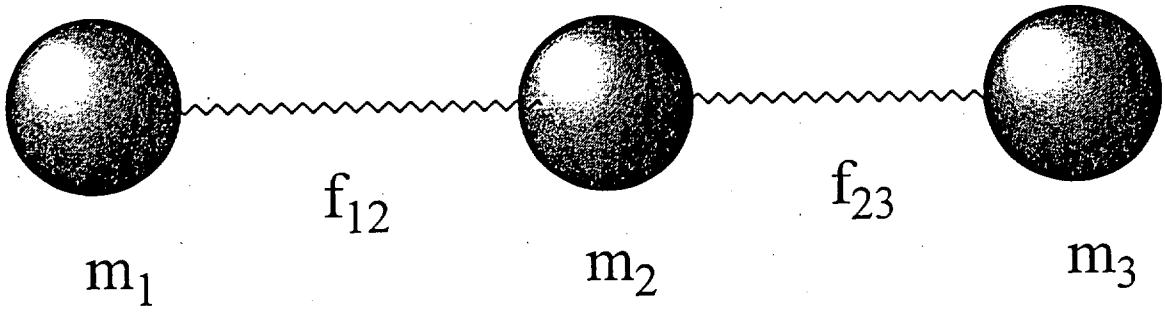
Supplementary Material

Three-Body Model

The three mass, spring model is:



The potential energy of the system is given by:

$$2V = f_{12}(\Delta r_{12})^2 + f_{23}(\Delta r_{23})^2$$

where $\Delta r_{12} = \Delta x_1 - \Delta x_2$ and $\Delta r_{23} = \Delta x_2 - \Delta x_3$ so that

$$2V = f_{12}(\Delta x_1 - \Delta x_2)^2 + f_{23}(\Delta x_2 - \Delta x_3)^2$$

or $2V = f_{12}(\Delta x_1)^2 + (f_{12} + f_{23})(\Delta x_2)^2 + f_{23}(\Delta x_3)^2 - 2f_{23}(\Delta x_2 \Delta x_3) - 2f_{12}(\Delta x_1 \Delta x_2)$

The kinetic energy is

$$2T = m_1(\Delta x_1)^2 + m_2(\Delta x_2)^2 + m_3(\Delta x_3)^2$$

The equations of motion are then:

$$m_1(\Delta x_1)^{..} + f_{12}(\Delta x_1) - f_{12}(\Delta x_2) = 0$$

$$m_2(\Delta x_2)^{..} + (f_{12} + f_{23})(\Delta x_2) - f_{23}(\Delta x_3) - f_{12}(\Delta x_1) = 0$$

$$m_3(\Delta x_3)^{..} + f_{23}(\Delta x_3) - f_{23}(\Delta x_2) = 0$$

The substitution

$$\Delta x_j = A_j \cos(\sqrt{\lambda} t + \varepsilon)$$

leads to the equations

$$(f_{12} - m_1\lambda)A_1 - f_{12} A_2 = 0$$

$$-f_{12} A_1 + (f_{12} + f_{23} - m_2\lambda)A_2 - f_{23} A_3 = 0$$

$$(f_{23} - m_3\lambda)A_3 - f_{23} A_2 = 0$$

The equations have non-zero solutions only if the determinant of the coefficients vanishes:

$$\begin{vmatrix} (f_{12} - m_1\lambda) & -f_{12} & 0 \\ -f_{12} & (f_{12} + f_{23} - m_2\lambda) & -f_{23} \\ 0 & -f_{23} & (f_{23} - m_3\lambda) \end{vmatrix}$$

$\lambda=0$ is one eigenvalue because there are only two force constants.

$$- m_1m_3m_2\lambda^2 + ((m_1 + m_2)m_3f_{12} + (m_2 + m_3)m_1f_{23})\lambda - (m_1 + m_2 + m_3)f_{12}f_{23} = 0$$

which has the solution

$$\lambda = \frac{\left(\left(m_1+m_2\right)m_3f_{12}+\left(m_2+m_3\right)m_1f_{23}\right) \pm \sqrt{\left(\left(m_1+m_2\right)m_3f_{12}+\left(m_2+m_3\right)m_1f_{23}\right)^2 - 4m_1m_2m_3\left(m_1+m_2+m_3\right)}}{2m_1m_2m_3}$$

In the special case where the force constants are equal:

$$- m_1m_3m_2\lambda^2 + f(m_2m_3 + m_1m_2 + 2m_1m_3)\lambda - f^2(m_1 + m_2 + m_3) = 0$$

the result is

$$\lambda = f\frac{\left(m_2m_3+m_1m_2+2m_1m_3\right) \pm \sqrt{m_2^2m_3^2+m_1^2m_2^2+4m_1^2m_3^2-2m_1m_2^2m_3}}{2m_1m_2m_3}$$

Our three-body masses are:
m1 = 488 a.m.u
m2 = 56 a.m.u
m_3 = 68 a.m.u

It would be possible for the observed vibrational mode to be either (+) predominantly 12 or (-) predominantly 23 combination. For example, assuming f = 3.36 mdyne/Å the two normal modes in this analysis have frequencies of 507.3 (+) and 203.7 (-).

A table of isotope effects for three body model with identical force constants of 3.36 mdyne/Å are given below (Table A1). This result can be compared to the two body model (again with f = 3.36 mdyne/Å). For a two-body model $1/\mu = (m_1 + m_2)/m_1m_2 = 0.0325$ and the frequency is 431.0 cm^{-1} for this foce constant. The three-body model presented with 3.36 mdyne/ Å for the axial ligand mode is acceptable

provided that the observed mode is the (-) combination. Notice that the pattern of isotope shifts is that shifts on the iron are smaller and imidazole are larger for the (-) combination. Neither this nor the fact that the (+) combination should also be observed are consistent with the data on the iron-axial-ligand stretching mode in heme proteins.

Table A1. Isotope effects calculated for a three-body model with two identical force constants of 3.36 mdyne/ Å

	$1/\mu$	$1/\mu$	$sq(\mu'/\mu)-1$	$\Delta\nu$	$sq(\mu'/\mu)-1$	$\Delta\nu$
Mode	(+)	(-)	(+)	507 cm^{-1}	(-)	203 cm^{-1}
Na	0.045180	0.0072893	0.0000	------	0.000	------
$4N_p$ on P	0.045174	0.0072782	-6.64 E -5	-0.033	-7.61 E -4	-0.15
d_3 Im	0.044767	0.0070801	-0.0040	-2.02	-0.0144	-2.92
di-^{15}N Im	0.044901	0.0071483	-0.0031	-1.57	-0.00971	-1.97
^{54}Fe	0.046466	0.0073260	0.0141	-7.16	0.00251	-0.509
^{57}Fe	0.044572	0.0072710	-0.0067	3.39	-0.0012	0.24

Since this result is not acceptable the relative frequencies of the two modes for different values of the force constant f are compared in Table A2.

Table A2. Isotope effects calculated for a three-body model with two identical force constant. The calculation is shown as a function of the force constant given in the first column.

f	(+)	(-)
(mdyne/Å)	(cm^{-1})	(cm^{-1})
3.36	507.3	203.7
1.67	358.0	143.8
0.7	231.7	93.0
0.66	224.8	88.6

The calculation with force constants of 0.66 mdyne/Å has the closest agreement with experiment in terms of the frequency of the (+) combination mode. The isotope effect can be readily calculated for the most acceptable values as shown in Table A3.

Table A3. Isotope effects for the three-body model calculation with two identical force constant of 0.66 mdyne/ Å.

	$1/\mu$	$1/\mu$	$sq(\mu'/\mu)-1$	$\Delta\nu$	$sq(\mu'/\mu)-1$	$\Delta\nu$
Mode	(+)	(-)	(+)	225 cm^{-1}	(-)	88.6cm^{-1}
Na	0.045180	0.0072893	0.0000	------	0.000	------
$4N_p$ on P	0.045174	0.0072782	-6.64 E -5	-0.022	-7.61 E -4	-0.06
d_3 Im	0.044767	0.0070801	-0.0040	-0.9	-0.0144	-1.3
di-^{15}N Im	0.044901	0.0071483	-0.0031	-0.7	-0.00971	-0.9
^{54}Fe	0.046466	0.0073260	0.0141	-3.2	0.00251	-0.22
^{57}Fe	0.044572	0.0072710	-0.0067	1.5	-0.0012	0.1

Using the approximation of identical force constants for the two internal stretching coordinates of the three-body model shown in Figure 1A, we can calculate the percent potential energy distribution (%PED) as follows.

Beginning with the definition of equations for the linear coefficient A_j and equating $f_{12} = f_{23} = f$, we have

$(f - m_1\lambda)A_1 - fA_2 = 0$
$-f A_1 + (2f - m_2\lambda)A_2 - fA_3 = 0$
$(f - m_3\lambda)A_3 - fA_2 = 0$

We found eigenvalues of $\lambda = 0.045$ and 0.007 for the (+) and (-) solutions, respectively.

Thus, for a given force constant and λ we can solve for the ratio of A_1 and A_3 to A_2.

for $\lambda = 0.007$
we have for the (-) combination

$A_1 = [f/(f - m_1\lambda_-)]A_2 = f/(f\text{-}0.007*488)\ A_2 = K_- A_2$
$A_3 = [f/(f - m_3\lambda_-)]A_2 = f/(f\text{-}0.007*68)\ A_2 = J_- A_2$

for $\lambda = 0.045$
we have for the (+) combination

$A_1 = [f/(f - m_1\lambda_+)]A_2 = f/(f\text{-}0.045*488)\ A_2 = K_+ A_2$
$A_3 = [f/(f - m_3\lambda_+)]A_2 = f/(f\text{-}0.045*68)\ A_2 = J_+ A_2$

The potential energy is given by $V = \frac{1}{2}[f_{12}(\Delta x_1 - \Delta x_2)^2 + f_{23}(\Delta x_2 - \Delta x_3)^2]$ so that we can define the total potential energy as $V = \frac{1}{2}[f(\Delta x_1 - \Delta x_2)^2 + f(\Delta x_2 - \Delta x_3)^2]$ for the equal force constant model discussed here. Substituting in the above information in terms of unnormalized displacements we have:
$V = \frac{1}{2}[f([K - 1]A_2)^2 + f([J - 1]A_2)^2]$ where $A_1 = KA_2$ and $A_3 = JA_2$.
The %PED for either of the coordinates is given by:

$$\frac{100*(K-1)^2}{[(K-1)^2+(J-1)^2]}$$

So that we can calculate for the models above that the %PEDs are given in table A4.

Table A4. Potential energy distributions for three-body model calculations.

f (mdyne/Å)	(+) Fe-L	(+) Fe-P	(-) Fe-L	(-) Fe-P
3.36	100.0	0.0	1.3	98.7
1.67	80.6	19.4	4.0	96.0
0.7	61.6	38.5	24.7	75.3
0.66	60.5	39.5	18.5	81.5

Several calculations were considered with variable force constants for the purpose of exploring the parameter space.

Case 1
$f_{12} = 3.36$
$f_{23} = 2.0$
Calculate numerically.
$\lambda = 0.01970$ and 0.11228 which corresponds to frequencies of 186.7 and 445.74 cm-1

	λ (+)	λ (-)	$\lvert(\lambda'/\lambda)-1$ (+)	ν $\Delta\nu$	$(\lambda'/\lambda)-1$ (-)	ν $\Delta\nu$
Na	0.11228	0.019700	----------	445.7 cm^{-1}	--------	99.9 cm^{-1}
^{15}Np	0.11225	0.019680	-1.3E-4	-0.06	-5.1 E-04	-0.09
d_3 Im	0.111645	0.019032	-0.0028	-1.24	-0.0171	-3.2
^{54}Fe	0.11577	0.019752	0.0154	6.9	0.0013	0.24

Case 2
$f_{12} = 1.0$
$f_{23} = 0.6$
Calculate numerically.
$\lambda = 0.005878$ and 0.033537 which corresponds to frequencies of 99.9 and 238.7 cm-1

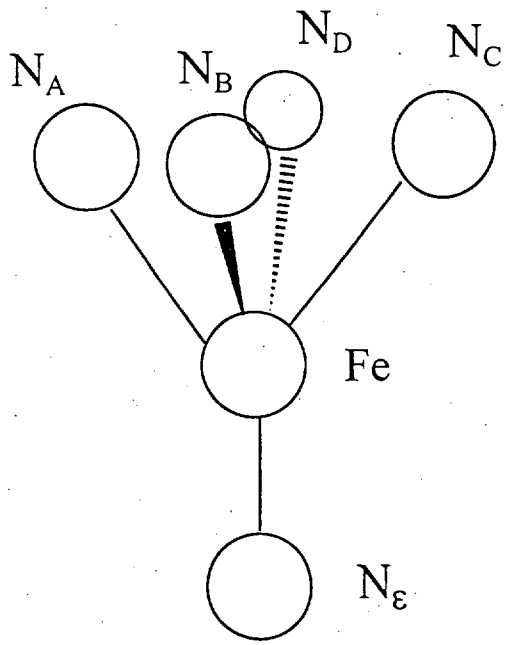
	λ (+)	λ (-)	$\lvert(\lambda'/\lambda)-1$ (+)	ν $\Delta\nu$	$(\lambda'/\lambda)-1$ (-)	ν $\Delta\nu$
Na	0.033537	0.005878	----------	238.7 cm^{-1}	--------	99.9 cm^{-1}
^{15}Np	0.033529	0.005871	-1.2E-04	-0.03	-6.0 E-04	-0.06
d_3 Im	0.033367	0.005701	-0.0025	-0.6	-0.015	-1.5
^{54}Fe	0.034588	0.005920	0.015	3.6	0.0035	0.356

Case 3
$f_{12} = 0.8$
$f_{23} = 0.6$
Calculate numerically.
λ = 0.005221 and 0.030216 which corresponds to frequencies of 96.1 and 231.2 cm-1.

	λ (+)	λ (-)	$\lvert(\lambda'/\lambda)-1$ (+)	ν $\Delta\nu$	$(\lambda'/\lambda)-1$ (-)	ν $\Delta\nu$
Na	0.030216	0.005221	----------	231.2 cm^{-1}	--------	96.1 cm^{-1}
^{15}Np	0.030211	0.005212	-8.3E-05	-0.02	-8.6 E-04	-0.08
d_3 Im	0.030017	0.005071	-0.0032	-0.74	-0.0145	-1.4
^{54}Fe	0.03109	0.005205	0.0143	3.30	0.0015	0.14

Six-body model

The six-body model for a heme-axial-ligand complex has C_{4v} symmetry. We treat the porphyrin ring as consisting of four pyrrole nitrogens (N_A,N_B, N_C, and N_D) of appropriate equivalent mass, one iron, and one axial atom with the equivalent mass of imidazole.



6 atoms x 3 degrees of freedom = 18 degrees of freedom

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
18	2	-2	4	2

$A_1 = (18 + 4 + -2 + 8 + 4)/8 = 4$

$A_2 = (18 + 4 - 2 - 8 - 4)/8 = 1$

$B_1 = (18 - 4 - 2 + 8 - 4)/8 = 2$

$B_2 = (18 - 4 - 2 - 8 + 4)/8 = 1$

$E = (36 + 0 + 4)/8 = 5$

$\Gamma = 4\ A_1 + 1\ A_2 + 2\ B_1 + 1\ B_2 + 5\ E$

For translation take away 1 E and 1 A_1

For rotation take away 1 E and 1 A_2

$\Gamma_{vib} = 3\ A_1 + 2\ B_1 + 1\ B_2 + 3\ E$ or 12 normal modes

$\Gamma_{Raman} = 3\ A_1 + 2\ B_1 + 1\ B_2 + 3\ E$

Definition of internal coordinates

Δd_A is the displacement of nitrogen A with respect to iron (etc.)

There are five total displacement internal coordinates.

$\Delta\theta_{AB}$ is the angle of N_A-Fe-N_B (etc.)

There are eight possible angles.

For the equatorial displacements

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
4	0	0	4	0

$\Gamma_{EqDis} = A_1 + B_1 + E$

For the axial displacement

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
1	1	1	1	1

$\Gamma_{AxDis} = A_1$

For the equatorial angles

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
4	0	0	0	4

$\Gamma_{EqAngle} = A_1 + B_2 + E$

For the axial angles

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
1	1	1	1	1

$\Gamma_{AxDis} = A_1$

For the equatorial angles

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
4	0	0	0	4

$\Gamma_{EqAngle} = A_1 + B_2 + E$

For the axial angles

E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
4	0	0	4	0

$\Gamma_{Ax\ Angle} = A_1 + B_1 + E$

Projection operators to generate symmetry coordinates for normal modes.

$P^{A1}\ \Delta\theta_{AB} = 1/2(\Delta\theta_{AB} + \Delta\theta_{CD} + \Delta\theta_{BC} + \Delta\theta_{DA})$

$P^{A1}\ \Delta d_A = 1/2(\Delta d_A + \Delta d_B + \Delta d_C + \Delta d_D)$

$P^{A1}\ \Delta d_X = \Delta d_X$

$P^{A1}\ \Delta\theta_{AX} = 1/2(\Delta\theta_{AX} + \Delta\theta_{BX} + \Delta\theta_{CX} + \Delta\theta_{DX})$

The two type of angle deformation have at least one redundant angle so $\Delta\theta_{DA}$ is removed.

$P^{B2}\ \Delta\theta_{AB} = 1/2(\Delta\theta_{AB} - \Delta\theta_{BC} + \Delta\theta_{CD} - \Delta\theta_{DA})$

$P^{B2}\ \Delta d_A = \Delta d_A - \Delta d_B + \Delta d_C - \Delta d_D = 0$

$P^{B2}\ \Delta d_X = 0$

$P^{B2}\ \Delta\theta_{AX} = \Delta\theta_{AX} - \Delta\theta_{BX} + \Delta\theta_{CX} - \Delta\theta_{DX} = 0$

$P^{B1}\ \Delta\theta_{AB} = 0$

$P^{B1}\ \Delta d_A = 1/2(\Delta d_A - \Delta d_B + \Delta d_C - \Delta d_D)$

$P^{B1}\ \Delta d_X = 0$

$P^{B1}\ \Delta\theta_{AX} = 1/2(\Delta\theta_{AX} - \Delta\theta_{BX} + \Delta\theta_{CX} - \Delta\theta_{DX})$

$P^{E}\ \Delta\theta_{AB} = 1/2^{1/2}(\Delta\theta_{AB} - \Delta\theta_{CD})$

$P^{E}\ \Delta\theta_{BC} = 1/2^{1/2}(\Delta\theta_{BC} - \Delta\theta_{DA})$

$P^{E}\ \Delta d_A = 1/2^{1/2}(\Delta d_A - \Delta d_C)$

$P^{E}\ \Delta d_B = 1/2^{1/2}(\Delta d_B - \Delta d_D)$

$P^{E}\ \Delta d_X = 0$

$P^{E}\ \Delta\theta_{AX} = 1/2^{1/2}(\Delta\theta_{AX} - \Delta\theta_{CX})$

$P^{E}\ \Delta\theta_{BX} = 1/2^{1/2}(\Delta\theta_{BX} - \Delta\theta_{DX})$

Based on these symmetry coordinates the **U**-matrix is:

$\Delta\theta_{AX}$	$\Delta\theta_{BX}$	$\Delta\theta_{CX}$	$\Delta\theta_{DX}$	$\Delta\theta_{AB}$	$\Delta\theta_{BC}$	$\Delta\theta_{CD}$	Δd_A	Δd_B	Δd_C	Δd_D	Δd_x
0	0	0	0	0	0	0	0	0	0	0	1
0	0	0	0	0	0	0	1/2	1/2	1/2	1/2	0
0	0	0	0	0	0	0	1/2	-1/2	1/2	-1/2	0
0	0	0	0	0	0	0	1/r2	0	-1/r2	0	0
0	0	0	0	0	0	0	0	1/r2	0	-1/r2	0
0	0	0	0	1/2	-1/2	1/2	0	0	0	0	0
0	0	0	0	1/r2	0	-1/r2	0	0	0	0	0
0	0	0	0	0	1/sr2	0	0	0	0	0	0
1/2	1/2	1/2	1/2	0	0	0	0	0	0	0	0
1/2	-1/2	1/2	-1/2	0	0	0	0	0	0	0	0
1/r2	0	-1/s2	0 0	0	0	0	0	0	0	0	0
0	1/r2	0	-1/r2	0	0	0	0	0	0	0	0

The **f**-matrix is:

$f_{\Delta\theta X}$	0	0	0	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	0	0	0
0	$f_{\Delta\theta X}$	0	0	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	0	0	0
0	0	$f_{\Delta\theta X}$	0	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	0	0	0
0	0	0	$f_{\Delta\theta X}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	0	0	0
$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta A}$	0	0	0	0	0	0	0	0
$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	$f_{\Delta\theta A}$	0	0	0	0	0	0	0
$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	$f_{\Delta\theta A}$	0	0	0	0	0	0
$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	$f_{\Delta\theta AX}$	0	0	0	$f_{\Delta\theta A}$	0	0	0	0	0
0	0	0	0	0	0	0	0	$f_{\Delta dA}$	0	0	0	$f_{\Delta dAX}$
0	0	0	0	0	0	0	0	0	$f_{\Delta dA}$	0	0	$f_{\Delta dAX}$
0	0	0	0	0	0	0	0	0	0	$f_{\Delta dA}$	0	$f_{\Delta dAX}$
0	0	0	0	0	0	0	0	0	0	0	$f_{\Delta dA}$	$f_{\Delta dAX}$
0	0	0	0	0	0	0	0	$f_{\Delta dAX}$	$f_{\Delta dAX}$	$f_{\Delta dAX}$	$f_{\Delta dAX}$	$f_{\Delta dX}$

The **U'** matrix is:

0	0	0	0	0	0	0	0	0	1/2	1/2	1/r2	0
0	0	0	0	0	0	0	0	0	1/2	-1/2	0	1/r2
0	0	0	0	0	0	0	0	0	1/2	1/2	-1/r2	0
0	0	0	0	0	0	0	0	0	1/2	-1/2	0	-1/r2
0	0	0	0	0	1/2	1/2	1/r2	0	0	0	0	0
0	0	0	0	0	1/2	-1/2	0	1/r2	0	0	0	0
0	0	0	0	0	1/2	1/2	-1/r2	0	0	0	0	0
0	0	0	0	0	1/2	-1/2	0	-1/r2	0	0	0	0
0	1/2	1/2	1/r2	0	0	0	0	0	0	0	0	
0	1/2	-1/2	0	1/r2	0	0	0	0	0	0	0	
0	1/2	1/2	-1/r2	0 0	0	0	0	0	0	0	0	
0	1/2	-1/2	0	-1/r2	0	0	0	0	0	0	0	
1	0	0	0	0	0	0	0	0	0	0	0	

The **F**-matrix is:

$f_{\Delta dX}$	$2f_{\Delta dAX}$	0	0	0	0	0	0	0	0	0	0	0
$2f_{\Delta dAX}$	$f_{\Delta dA}$	0	0	0	0	0	0	0	0	0	0	0
0	0	$f_{\Delta dA}$	0	0	0	0	0	0	0	0	0	0
0	0	0	$f_{\Delta dA}$	0	0	0	0	0	0	0	0	0
0	0	0	0	$f_{\Delta dA}$	0	0	0	0	0	0	0	0
0	0	0	0	0	$f_{\Delta\theta A}$	0	0	0	$4f_{\Delta\theta AX}$	0	0	0
0	0	0	0	0	0	$f_{\Delta\theta A}$	0	0	0	0	0	0
0	0	0	0	0	0	0	$f_{\Delta\theta A}$	0	0	0	0	0
0	0	0	0	0	0	0	0	$f_{\Delta\theta A}$	0	0	0	0
0	0	0	0	0	$4f_{\Delta\theta AX}$	0	0	0	$f_{\Delta\theta X}$	0	0	0
0	0	0	0	0	0	0	0	0	0	$f_{\Delta\theta X}$	0	0
0	0	0	0	0	0	0	0	0	0	0	$f_{\Delta\theta X}$	0
0	0	0	0	0	0	0	0	0	0	0	0	$f_{\Delta\theta X}$

We wish to calculate **G** = **UgU'** where **g** is:

	$\Delta\theta_{AX}$	$\Delta\theta_{BX}$	$\Delta\theta_{CX}$	$\Delta\theta_{DX}$	$\Delta\theta_{AB}$	$\Delta\theta_{BC}$	$\Delta\theta_{CD}$	$\Delta\theta_{DA}$	Δd_A	Δd_B	Δd_C	Δd_D	Δd_X
$\Delta\theta_{AX}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$
$\Delta\theta_{BX}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$
$\Delta\theta_{CX}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$
$\Delta\theta_{DX}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$
$\Delta\theta_{AB}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$
$\Delta\theta_{BC}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$
$\Delta\theta_{CD}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{\phi\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$
$\Delta\theta_{DA}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi'}^{1}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{2}$	$g_{\phi\phi}^{3}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$
Δd_A	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	g_{rr}^{2}	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$
Δd_B	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{rr'}^{1}$	g_{rr}^{2}	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$
Δd_C	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	g_{rr}^{2}	$g_{rr'}^{1}$	$g_{rr'}^{1}$
Δd_D	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	g_{rr}^{2}	$g_{rr'}^{1}$
Δd_X	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{2}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{r\phi}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	$g_{rr'}^{1}$	g_{rr}^{2}

The A_1 symmetry block is:

$f_{\Delta dX}$	$2f_{\Delta AX}$	0	0
$2f_{\Delta dAX}$	$f_{\Delta dA}$	0	0
0	0	$f_{\Delta\theta A}$	$4f_{\Delta\theta AX}$
0	0	$4f_{\Delta\theta AX}$	$f_{\Delta\theta X}$

g_{rr}^{2}	$2g_{rr'}^{1}$	$2g_{r\phi}^{1}$	$2g_{r\phi}^{2}$
$2g_{rr'}^{1}$	$g_{rr}^{2}+3g_{rr'}^{1}$	$2(g_{r\phi}^{1}+g_{r\phi}^{2})$	$g_{r\phi}^{2}+3g_{r\phi}^{1}$
$2g_{r\phi}^{1}$	$2(g_{r\phi}^{2}+g_{r\phi}^{1})$	$g_{\phi\phi}^{3}+3g_{\phi\phi}^{2}$	$4g_{\phi\phi'}^{1}$
$g_{r\phi}^{2}$	$g_{r\phi}^{2}+3g_{r\phi}^{1}$	$4g_{\phi\phi'}^{1}$	$g_{\phi\phi}^{3}+3g_{\phi\phi}^{2}$

We can eliminate the redundant coordinate at this point. It is $\Delta\theta A$.

$f_{\Delta dX}$	$2f_{\Delta AX}$	0
$2f_{\Delta dAX}$	$f_{\Delta dA}$	0
0	0	$f_{\Delta\theta X}$

1.67	0	0
0	1.67	0
0	0	0.83

g_{rr}^{2}	$2g_{rr'}^{1}$	$2g_{r\phi}^{2}$
$2g_{rr'}^{1}$	$g_{rr}^{2A}+3g_{rr'}^{1}$	$g_{r\phi}^{2A}+3g_{r\phi}^{1}$
$2g_{r\phi}^{2}$	$g_{r\phi}^{2A}+3g_{r\phi}^{1}$	$g_{\phi\phi}^{3}+3g_{\phi\phi}^{2}$

0.03255	-0.0068	-0.01668
-0.0068	0.01584	-0.008389
-0.01668	-0.008389	0.0149

for $f_{\Delta dX}$

$g_{rr}^{2} = \mu_1 + \mu_2 = 1/68 + 1/56 = (0.01470) + (0.01785) = 0.03255$

for $f_{\Delta dA}$

$g_{rr}^{2A} = \mu_3 + \mu_2 = 1/122 + 1/56 = (0.008196) + (0.01785) = 0.02604$

for $f_{\Delta dA}$ and $f_{\Delta dX}$

$g_{rr'}^{1} = \mu_2 \cos\phi = 1/56 \cos(101.04) = (0.01785)(-0.191) = -0.0034$

for $f_{\Delta dA}$ and $f_{\Delta\theta X}$

$g_{r\phi}^{1} = \rho_{13}\, \mu_3 \sin\phi \cos\tau = 0$

for $f_{\Delta dX}$ and $f_{\Delta\theta X}$

$g_{r\phi}^2 = -\rho_{23}\,\mu_2 \sin\phi = -(1/2.1)(1/56)\sin(101.04) = -(0.4761)(0.01785)(0.981) = -0.008340$

for $f_{\Delta dA}$ and $f_{\Delta\theta X}$

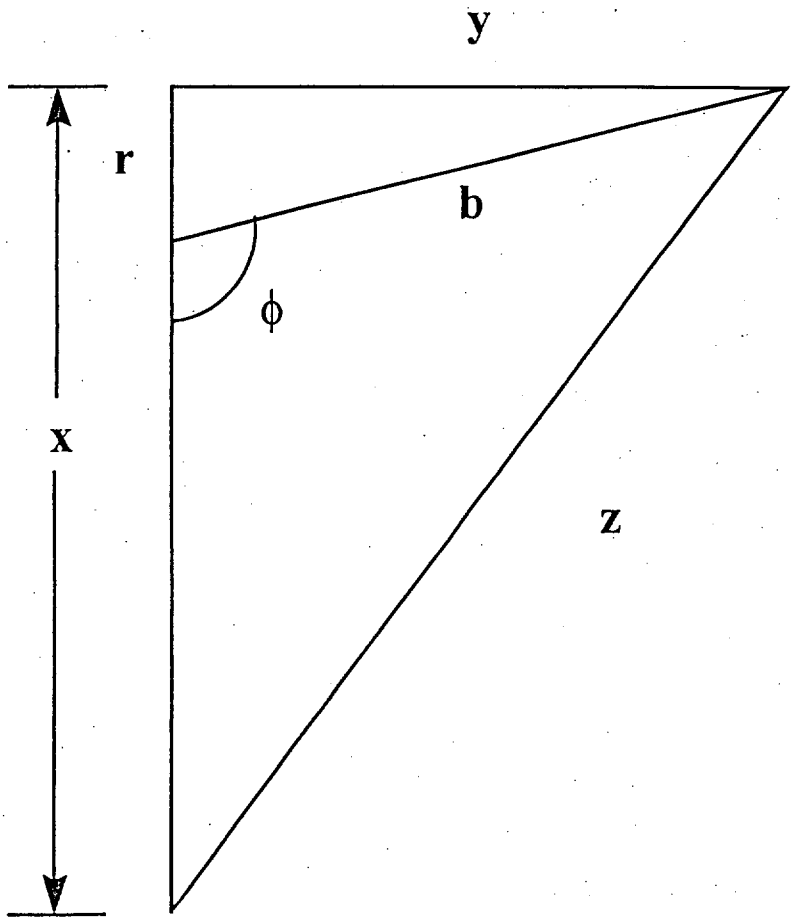
$g_{r\phi}^{2A} = -\rho_{12}\,\mu_2 \sin\phi = -(1/2.088)(1/56)\sin(101.04) = -(0.4789)(0.01785)(0.981) = -0.008389$

for $f_{\Delta\theta X}$

$g_{\phi\phi}^3 = \rho_{12}^2\mu_1 + \rho_{23}^2\,\mu_3 + (\rho_{12}^2 + \rho_{23}^2 - 2\rho_{12}\rho_{23}\cos\phi)\mu_2 = (1/122)(1/2.088)^2 + (1/68)(1/2.1)^2 -$
$(0.008196)(0.2293) + (0.01470)(0.2267) + (0.2293 + 0.2267 - 0.4561\,(-0.191))(0.01785) = 0.01490$

$g_{\phi\phi'}^2 = 0$ because the dihedral angle between the planes is 90 degrees and therefore cos τ is zero.

Make the following identifications.
1 = pyrrole nitrogens
2 = iron
3 = axial ligand



r is the iron doming coordinate (i.e. relative to the plane of the pyrrole nitrogens)
Note that $\phi = \pi - \eta$ where η = arccos r/b.or arctan y/r
In fact the length x and z are irrelevant for determination of the angle.

So if y = 2.05 Å and r = 0.4 Å then y/r = 5.125
η = 78.959
ϕ = 101.04

$\cos\phi$ = -0.191
$\sin\phi$ = 0.981

Assuming that x = 2.5 Å then b = $\sqrt{(r^2 + y^2)}$ = 2.088 Å
x = 2.5 Å means that the iron axial ligand bond is 2.1 Å.

$f_{\Delta dX}$	$2f_{\Delta AX}$	0
$2f_{\Delta dAX}$	$f_{\Delta dA}$	0
0	0	$f_{\Delta\theta X}$

g_{rr}^2	$2g_{rr'}^1$	$2g_{r\phi}^2$
$2g_{rr'}^1$	$g_{rr}^{2A}+3g_{rr'}^1$	$g_{r\phi}^{2A}$
$g_{r\phi}^2$	$g_{r\phi}^{2A}$	$g_{\phi\phi}^3$

The FG Matrix is the product of these two.

The 38-body model

Although the addition of interaction force constants and torsional force constants could be used to refine the force field we find that this is not warranted. We present no quantitative conclusions for such modeling because there is no justification for introducing a greater number of parameters based on the present experimental data. Qualitatively, the effect of introducing out-of-plane force constants (3) is to introduce significant mixing of porphyrin doming and ruffling coordinates into the normal modes that involve the iron-axial-ligand stretch. If the motion of the axial ligand is purely axial then the ruffling coordinate does not contribute by symmetry, however, ruffling can cause mixing of nominally in-plane internal coordinates with off-axis tilting of the ligand. By including these internal coordinates the pyrrole ^{15}N isotope effect begins to become much larger than the values of 0.2 - 0.4 cm^{-1} for modes A and B shown in Table 6. The experimental data rule out larger isotope effects. The recent observation that proteins enforce distortions along the low frequency saddling, ruffling, and doming vibrational modes suggests a significant constraint exists on these degrees of freedom. (2) It is possible that torsional degrees of freedom in crystal or solution may be significantly different than in proteins. Our results suggest that porphyrin torsions would almost necessarily lead to an isotope effect for ^{15}N substituted porphyrins in myoglobin, contrary to experimental observation. (1) The view of the iron-axial-ligand mode that emerges from our analysis is

of a structurally rigid porphyrin with significant ligand bending in a mode that is approximately 50% an iron-ligand stretch.

The experimental evidence for a protein role in enforcing distortions of metalloporphyrins has been presented. The globins (including H93G myoglobin studied here) have a known domed structure that is enforced by the protein and the interplay between protein structure in the R and T state of hemoglobins. The domed heme of the T state lowers the iron-histidine mode frequency. The lowering of the frequency may occur due to off-axis tilting that increases anharmonic coupling to low frequency bending modes. It is remarkable that the frequency lowering in the T state of two different types of hemoglobins are similar in spite of different mechanisms for enforcing the T state. (4) This observations suggests a key role for the heme geometry. Peroxidases have an enforced saddled conformation of the heme and this may affect the mixing of the porphyrin out-of-plane modes and axial-ligand stretching. (2) These examples serve to indicate the importance of structural constraints on out-of-plane torsional and wagging internal coordinates.

The 38-body model applied here uses the SVIB program available from the Quantum Chemistry Program Exchange. The parameters used in a representative input file are given below. No hydrogens are included. The carbons in the imidazole ring were pseudo-atoms with a mass of 13 a.m.u. (carbon plus hydrogen). The eight peripheral substituents in the β-position are pseudo-atoms with a mass 24 a.m.u. This number was chosen for consistency with the three-body and six-body models and represents an average number for the methyl, vinyl, and propionate substituents of heme. The parameters that were varied systematically in the model calculations are shown in bold in the input file. The masses were altered to model the isotope effect. For example, the pyrrole nitrogen isotope effect was modeled by replacing:

```
XMATRX      3  2.027970 -0.077730 -0.115320 14.000000 NA___
XMATRX      4 -0.043490 -2.101650 -0.245570 14.000000 NB___
XMATRX      5 -2.058600 -0.028090 -0.430350 14.000000 NC___
XMATRX      6  0.015760  1.998760 -0.300210 14.000000 ND___
```

with

```
XMATRX      3  2.027970 -0.077730 -0.115320 15.000000 NA___
XMATRX      4 -0.043490 -2.101650 -0.245570 15.000000 NB___
XMATRX      5 -2.058600 -0.028090 -0.430350 15.000000 NC___
XMATRX      6  0.015760  1.998760 -0.300210 15.000000 ND___
```

Sample input file for SVIB

```
************************************************************
SPV_VERSION 100
HEADER
```

```
COMPND im_heme_model
ISOTOP Na__
REMARK File created by franzen on Tue Apr 29 15:14:36 PDT 1997
COMMENT     #  Xcoord    Ycoord    Zcoord   AtomMass  Atomtype
XMATRX      1 -0.031260 -0.049220 -0.056900 56.000000 FE___
XMATRX      2 -0.191350 -0.019700  2.027460 14.000000 NX___
XMATRX      3  2.027970 -0.077730 -0.115320 14.000000 NA___
XMATRX      4 -0.043490 -2.101650 -0.245570 14.000000 NB___
XMATRX      5 -2.058600 -0.028090 -0.430350 14.000000 NC___
XMATRX      6  0.015760  1.998760 -0.300210 14.000000 ND___
XMATRX      7  2.819680 -1.194340 -0.082010 12.000000 C1___
XMATRX      8  4.196500 -0.793220  0.032530 12.000000 C2___
XMATRX      9  4.220420  0.556410  0.070200 12.000000 C3___
XMATRX     10  2.858520  1.012740 -0.063270 12.000000 C4___
XMATRX     11  2.372150 -2.507660 -0.137740 12.000000 C5___
XMATRX     12 -1.153830 -2.902510 -0.324430 12.000000 C6___
XMATRX     13 -0.738120 -4.282420 -0.267610 12.000000 C7___
XMATRX     14  0.612230 -4.295360 -0.228850 12.000000 C8___
XMATRX     15  1.050500 -2.925130 -0.202400 12.000000 C9___
XMATRX     16 -2.462830 -2.451130 -0.456250 12.000000 C1__0
XMATRX     17 -2.843870  1.086340 -0.558280 12.000000 C1__1
XMATRX     18 -4.219420  0.675860 -0.682070 12.000000 C1__2
XMATRX     19 -4.245320 -0.679980 -0.707970 12.000000 C1__3
XMATRX     20 -2.882560 -1.123260 -0.518070 12.000000 C1__4
XMATRX     21 -2.387760  2.400640 -0.575130 12.000000 C1__5
XMATRX     22  1.134190  2.791280 -0.256680 12.000000 C1__6
XMATRX     23  0.730870  4.171100 -0.348380 12.000000 C1__7
XMATRX     24 -0.613730  4.197390 -0.524750 12.000000 C1__8
XMATRX     25 -1.066260  2.825680 -0.461960 12.000000 C1__9
XMATRX     26  2.445540  2.338450 -0.138220 24.000000 C2__0
XMATRX     27  0.526410  0.750420  2.860610 13.000000 C2__9
XMATRX     28  0.148630  0.492430  4.122550 15.000000 NY___
XMATRX     29 -0.811120 -0.442810  4.093050 13.000000 C3__0
XMATRX     30 -1.027190 -0.768080  2.761230 13.000000 C3__1
XMATRX     31 -1.630010 -5.472330 -0.311000 24.000000 C2__1
XMATRX     32  5.431970  1.413520  0.169420 24.000000 C2__2
XMATRX     33  1.643290  5.345680 -0.255670 24.000000 C2__3
XMATRX     34 -5.391020  1.593650 -0.759170 24.000000 C2__4
XMATRX     35 -1.439490  5.283660 -0.715290 24.000000 C2__5
XMATRX     36 -5.324950 -1.521150 -0.865910 24.000000 C2__6
XMATRX     37  1.501520 -5.496590 -0.175850 24.000000 C2__7
XMATRX     38  5.357390 -1.726490  0.154370 24.000000 C2__8
COMMENT     #    Atom Numbers of connected atoms
CONECT      1    4    3    6    5    2    0
CONECT      2    1   27   30    0    0    0
CONECT      3    1    7   10    0    0    0
CONECT      4    1   12   15    0    0    0
CONECT      5    1   17   20    0    0    0
CONECT      6    1   22   25    0    0    0
CONECT      7    3    8   11    0    0    0
CONECT      8    7    9   38    0    0    0
CONECT      9    8   10   32    0    0    0
CONECT     10    3    9   26    0    0    0
CONECT     11    7   15    0    0    0    0
CONECT     12    4   13   16    0    0    0
CONECT     13   12   14   31    0    0    0
CONECT     14   13   15   37    0    0    0
CONECT     15    4   11   14    0    0    0
CONECT     16   12   20    0    0    0    0
CONECT     17    5   18   21    0    0    0
```

```
CONECT   18   17   19   34    0    0    0
CONECT   19   18   20   36    0    0    0
CONECT   20    5   16   19    0    0    0
CONECT   21   17   25    0    0    0    0
CONECT   22    6   23   26    0    0    0
CONECT   23   22   24   33    0    0    0
CONECT   24   23   25   35    0    0    0
CONECT   25    6   21   24    0    0    0
CONECT   26   10   22    0    0    0    0
CONECT   27    2   28    0    0    0    0
CONECT   28   27   29    0    0    0    0
CONECT   29   28   30    0    0    0    0
CONECT   30    2   29    0    0    0    0
CONECT   31   13    0    0    0    0    0
CONECT   32    9    0    0    0    0    0
CONECT   33   23    0    0    0    0    0
CONECT   34   18    0    0    0    0    0
CONECT   35   24    0    0    0    0    0
CONECT   36   19    0    0    0    0    0
CONECT   37   14    0    0    0    0    0
CONECT   38    8    0    0    0    0    0
COMMENT    #  ForceConstant LowerBound Upperbound DescriptiveLabel
DIF_FC     1  6.980    0.000    0.000 K(C10C14)
DIF_FC     2  6.980    0.000    0.000 K(C10C6_)
DIF_FC     3  5.430    0.000    0.000 K(C11C12)
DIF_FC     4  6.980    0.000    0.000 K(C11C15)
DIF_FC     5  5.640    0.000    0.000 K(C11NC_)
DIF_FC     6  7.120    0.000    0.000 K(C12C13)
DIF_FC     7  4.200    0.000    0.000 K(C12C24)
DIF_FC     8  5.430    0.000    0.000 K(C13C14)
DIF_FC     9  4.200    0.000    0.000 K(C13C26)
DIF_FC    10  5.640    0.000    0.000 K(C14NC_)
DIF_FC    11  6.980    0.000    0.000 K(C15C19)
DIF_FC    12  5.430    0.000    0.000 K(C16C17)
DIF_FC    13  6.980    0.000    0.000 K(C16C20)
DIF_FC    14  5.640    0.000    0.000 K(C16ND_)
DIF_FC    15  7.120    0.000    0.000 K(C17C18)
DIF_FC    16  4.200    0.000    0.000 K(C17C23)
DIF_FC    17  5.430    0.000    0.000 K(C18C19)
DIF_FC    18  4.200    0.000    0.000 K(C18C25)
DIF_FC    19  5.640    0.000    0.000 K(C19ND_)
DIF_FC    20  5.430    0.000    0.000 K(C1_C2_)
DIF_FC    21  6.980    0.000    0.000 K(C1_C5_)
DIF_FC    22  5.640    0.000    0.000 K(C1_NA_)
DIF_FC    23  6.980    0.000    0.000 K(C20C4_)
DIF_FC    24  4.200    0.000    0.000 K(C21C7_)
DIF_FC    25  4.200    0.000    0.000 K(C22C3_)
DIF_FC    26  4.200    0.000    0.000 K(C27C8_)
DIF_FC    27  4.200    0.000    0.000 K(C28C2_)
DIF_FC    28  7.560    0.000    0.000 K(C29NX_)
DIF_FC    29  6.060    0.000    0.000 K(C29NY_)
DIF_FC    30  7.120    0.000    0.000 K(C2_C3_)
DIF_FC    31  8.130    0.000    0.000 K(C30C31)
DIF_FC    32  5.300    0.000    0.000 K(C30NY_)
DIF_FC    33  5.070    0.000    0.000 K(C31NX_)
DIF_FC    34  5.430    0.000    0.000 K(C3_C4_)
DIF_FC    35  5.640    0.000    0.000 K(C4_NA_)
DIF_FC    36  6.980    0.000    0.000 K(C5_C9_)
DIF_FC    37  5.430    0.000    0.000 K(C6_C7_)
DIF_FC    38  5.640    0.000    0.000 K(C6_NB_)
```

```
DIF_FC   39  7.120   0.000   0.000 K(C7_C8_)
DIF_FC   40  5.430   0.000   0.000 K(C8_C9_)
DIF_FC   41  5.640   0.000   0.000 K(C9_NB_)
DIF_FC   42  1.000   0.000   0.000 K(FE_NA_)
DIF_FC   43  1.000   0.000   0.000 K(FE_NB_)
DIF_FC   44  1.000   0.000   0.000 K(FE_NC_)
DIF_FC   45  1.000   0.000   0.000 K(FE_ND_)
DIF_FC   46  1.000   0.000   0.000 K(FE_NX_)
DIF_FC   47  0.830   0.000   0.000 H(C10C14C13)
DIF_FC   48  0.830   0.000   0.000 H(C10C14NC_)
DIF_FC   49  0.830   0.000   0.000 H(C10C6_C7_)
DIF_FC   50  0.830   0.000   0.000 H(C10C6_NB_)
DIF_FC   51  1.370   0.000   0.000 H(C11C12C13)
DIF_FC   52  1.200   0.000   0.000 H(C11C12C24)
DIF_FC   53  1.100   0.000   0.000 H(C11C15C19)
DIF_FC   54  1.620   0.000   0.000 H(C11NC_C14)
DIF_FC   55  0.300   0.000   0.000 H(C11NC_FE_)
DIF_FC   56  0.830   0.000   0.000 H(C12C11C15)
DIF_FC   57  1.370   0.000   0.000 H(C12C11NC_)
DIF_FC   58  1.370   0.000   0.000 H(C12C13C14)
DIF_FC   59  1.200   0.000   0.000 H(C12C13C26)
DIF_FC   60  1.200   0.000   0.000 H(C13C12C24)
DIF_FC   61  1.370   0.000   0.000 H(C13C14NC_)
DIF_FC   62  1.100   0.000   0.000 H(C14C10C6_)
DIF_FC   63  1.200   0.000   0.000 H(C14C13C26)
DIF_FC   64  0.300   0.000   0.000 H(C14NC_FE_)
DIF_FC   65  0.830   0.000   0.000 H(C15C11NC_)
DIF_FC   66  0.830   0.000   0.000 H(C15C19C18)
DIF_FC   67  0.830   0.000   0.000 H(C15C19ND_)
DIF_FC   68  1.370   0.000   0.000 H(C16C17C18)
DIF_FC   69  1.200   0.000   0.000 H(C16C17C23)
DIF_FC   70  1.100   0.000   0.000 H(C16C20C4_)
DIF_FC   71  1.620   0.000   0.000 H(C16ND_C19)
DIF_FC   72  0.300   0.000   0.000 H(C16ND_FE_)
DIF_FC   73  0.830   0.000   0.000 H(C17C16C20)
DIF_FC   74  1.370   0.000   0.000 H(C17C16ND_)
DIF_FC   75  1.370   0.000   0.000 H(C17C18C19)
DIF_FC   76  1.200   0.000   0.000 H(C17C18C25)
DIF_FC   77  1.200   0.000   0.000 H(C18C17C23)
DIF_FC   78  1.370   0.000   0.000 H(C18C19ND_)
DIF_FC   79  1.200   0.000   0.000 H(C19C18C25)
DIF_FC   80  0.300   0.000   0.000 H(C19ND_FE_)
DIF_FC   81  1.200   0.000   0.000 H(C1_C2_C28)
DIF_FC   82  1.370   0.000   0.000 H(C1_C2_C3_)
DIF_FC   83  1.100   0.000   0.000 H(C1_C5_C9_)
DIF_FC   84  1.620   0.000   0.000 H(C1_NA_C4_)
DIF_FC   85  0.300   0.000   0.000 H(C1_NA_FE_)
DIF_FC   86  0.830   0.000   0.000 H(C20C16ND_)
DIF_FC   87  0.830   0.000   0.000 H(C20C4_C3_)
DIF_FC   88  0.830   0.000   0.000 H(C20C4_NA_)
DIF_FC   89  1.200   0.000   0.000 H(C21C7_C6_)
DIF_FC   90  1.200   0.000   0.000 H(C21C7_C8_)
DIF_FC   91  1.200   0.000   0.000 H(C22C3_C2_)
DIF_FC   92  1.200   0.000   0.000 H(C22C3_C4_)
DIF_FC   93  1.200   0.000   0.000 H(C27C8_C7_)
DIF_FC   94  1.200   0.000   0.000 H(C27C8_C9_)
DIF_FC   95  1.200   0.000   0.000 H(C28C2_C3_)
DIF_FC   96  1.200   0.000   0.000 H(C29NX_C31)
DIF_FC   97  1.200   0.000   0.000 H(C29NX_FE_)
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DIF_FC    98  1.200    0.000    0.000 H(C29NY_C30)
DIF_FC    99  0.830    0.000    0.000 H(C2_C1_C5_)
DIF_FC   100  1.370    0.000    0.000 H(C2_C1_NA_)
DIF_FC   101  1.370    0.000    0.000 H(C2_C3_C4_)
DIF_FC   102  1.620    0.000    0.000 H(C30C31NX_)
DIF_FC   103  1.370    0.000    0.000 H(C31C30NY_)
DIF_FC   104  0.300    0.000    0.000 H(C31NX_FE_)
DIF_FC   105  1.370    0.000    0.000 H(C3_C4_NA_)
DIF_FC   106  0.300    0.000    0.000 H(C4_NA_FE_)
DIF_FC   107  1.370    0.000    0.000 H(C5_C1_NA_)
DIF_FC   108  0.830    0.000    0.000 H(C5_C9_C8_)
DIF_FC   109  0.830    0.000    0.000 H(C5_C9_NB_)
DIF_FC   110  1.370    0.000    0.000 H(C6_C7_C8_)
DIF_FC   111  1.620    0.000    0.000 H(C6_NB_C9_)
DIF_FC   112  0.300    0.000    0.000 H(C6_NB_FE_)
DIF_FC   113  1.370    0.000    0.000 H(C7_C6_NB_)
DIF_FC   114  1.370    0.000    0.000 H(C7_C8_C9_)
DIF_FC   115  1.370    0.000    0.000 H(C8_C9_NB_)
DIF_FC   116  0.300    0.000    0.000 H(C9_NB_FE_)
DIF_FC   117  0.250    0.000    0.000 H(NA_FE_NB_)
DIF_FC   118  0.250    0.000    0.000 H(NA_FE_ND_)
DIF_FC   119  0.300    0.000    0.000 H(NA_FE_NX_)
DIF_FC   120  0.250    0.000    0.000 H(NB_FE_NC_)
DIF_FC   121  0.300    0.000    0.000 H(NB_FE_NX_)
DIF_FC   122  0.250    0.000    0.000 H(NC_FE_ND_)
DIF_FC   123  0.300    0.000    0.000 H(NC_FE_NX_)
DIF_FC   124  0.300    0.000    0.000 H(ND_FE_NX_)
DIF_FC   125  1.400    0.000    0.000 H(NX_C29NY_)
COMMENT    # Typ IC1 IC2 At1 At2 At3 At4At5 At6 At7 At8  ScaleF   FC#
Not.used.
FMATRX     1   1   1   1  16- 20   0   0   0   0   0   0 1.0000     1
K(C10C14)
FMATRX     2   1   2   2  12- 16   0   0   0   0   0   0 1.0000     2
K(C10C6_)
FMATRX     3   1   3   3  17- 18   0   0   0   0   0   0 1.0000     3
K(C11C12)
FMATRX     4   1   4   4  17- 21   0   0   0   0   0   0 1.0000     4
K(C11C15)
FMATRX     5   1   5   5   5- 17   0   0   0   0   0   0 1.0000     5
K(C11NC_)
FMATRX     6   1   6   6  18- 19   0   0   0   0   0   0 1.0000     6
K(C12C13)
FMATRX     7   1   7   7  18- 34   0   0   0   0   0   0 1.0000     7
K(C12C24)
FMATRX     8   1   8   8  19- 20   0   0   0   0   0   0 1.0000     8
K(C13C14)
FMATRX     9   1   9   9  19- 36   0   0   0   0   0   0 1.0000     9
K(C13C26)
FMATRX    10   1  10  10   5- 20   0   0   0   0   0   0 1.0000    10
K(C14NC_)
FMATRX    11   1  11  11  21- 25   0   0   0   0   0   0 1.0000    11
K(C15C19)
FMATRX    12   1  12  12  22- 23   0   0   0   0   0   0 1.0000    12
K(C16C17)
FMATRX    13   1  13  13  22- 26   0   0   0   0   0   0 1.0000    13
K(C16C20)
FMATRX    14   1  14  14   6- 22   0   0   0   0   0   0 1.0000    14
K(C16ND_)
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FMATRX   15   1  15  15  23- 24   0   0   0   0   0   0 1.0000   15
K(C17C18)
FMATRX   16   1  16  16  23- 33   0   0   0   0   0   0 1.0000   16
K(C17C23)
FMATRX   17   1  17  17  24- 25   0   0   0   0   0   0 1.0000   17
K(C18C19)
FMATRX   18   1  18  18  24- 35   0   0   0   0   0   0 1.0000   18
K(C18C25)
FMATRX   19   1  19  19   6- 25   0   0   0   0   0   0 1.0000   19
K(C19ND_)
FMATRX   20   1  20  20   7-  8   0   0   0   0   0   0 1.0000   20
K(C1_C2_)
FMATRX   21   1  21  21   7- 11   0   0   0   0   0   0 1.0000   21
K(C1_C5_)
FMATRX   22   1  22  22   3-  7   0   0   0   0   0   0 1.0000   22
K(C1_NA_)
FMATRX   23   1  23  23  10- 26   0   0   0   0   0   0 1.0000   23
K(C20C4_)
FMATRX   24   1  24  24  13- 31   0   0   0   0   0   0 1.0000   24
K(C21C7_)
FMATRX   25   1  25  25   9- 32   0   0   0   0   0   0 1.0000   25
K(C22C3_)
FMATRX   26   1  26  26  14- 37   0   0   0   0   0   0 1.0000   26
K(C27C8_)
FMATRX   27   1  27  27   8- 38   0   0   0   0   0   0 1.0000   27
K(C28C2_)
FMATRX   28   1  28  28   2- 27   0   0   0   0   0   0 1.0000   28
K(C29NX_)
FMATRX   29   1  29  29  27- 28   0   0   0   0   0   0 1.0000   29
K(C29NY_)
FMATRX   30   1  30  30   8-  9   0   0   0   0   0   0 1.0000   30
K(C2_C3_)
FMATRX   31   1  31  31  29- 30   0   0   0   0   0   0 1.0000   31
K(C30C31)
FMATRX   32   1  32  32  28- 29   0   0   0   0   0   0 1.0000   32
K(C30NY_)
FMATRX   33   1  33  33   2- 30   0   0   0   0   0   0 1.0000   33
K(C31NX_)
FMATRX   34   1  34  34   9- 10   0   0   0   0   0   0 1.0000   34
K(C3_C4_)
FMATRX   35   1  35  35   3- 10   0   0   0   0   0   0 1.0000   35
K(C4_NA_)
FMATRX   36   1  36  36  11- 15   0   0   0   0   0   0 1.0000   36
K(C5_C9_)
FMATRX   37   1  37  37  12- 13   0   0   0   0   0   0 1.0000   37
K(C6_C7_)
FMATRX   38   1  38  38   4- 12   0   0   0   0   0   0 1.0000   38
K(C6_NB_)
FMATRX   39   1  39  39  13- 14   0   0   0   0   0   0 1.0000   39
K(C7_C8_)
FMATRX   40   1  40  40  14- 15   0   0   0   0   0   0 1.0000   40
K(C8_C9_)
FMATRX   41   1  41  41   4- 15   0   0   0   0   0   0 1.0000   41
K(C9_NB_)
FMATRX   42   1  42  42   1-  3   0   0   0   0   0   0 1.0000   42
K(FE_NA_)
FMATRX   43   1  43  43   1-  4   0   0   0   0   0   0 1.0000   43
K(FE_NB_)
FMATRX   44   1  44  44   1-  5   0   0   0   0   0   0 1.0000   44
K(FE_NC_)
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FMATRX   45   1  45  45   1-  6   0   0  0  0  0  0  0  1.0000    45
K(FE_ND_)
FMATRX   46   1  46  46   1-  2   0   0  0  0  0  0  0  1.0000    46
K(FE_NX_)
FMATRX   47   2  47  47  16- 20- 19   0  0  0  0  0  0  1.0000    47
H(C10C14C13)
FMATRX   48   2  48  48   5- 20- 16   0  0  0  0  0  0  1.0000    48
H(C10C14NC_)
FMATRX   49   2  49  49  13- 12- 16   0  0  0  0  0  0  1.0000    49
H(C10C6_C7_)
FMATRX   50   2  50  50   4- 12- 16   0  0  0  0  0  0  1.0000    50
H(C10C6_NB_)
FMATRX   51   2  51  51  17- 18- 19   0  0  0  0  0  0  1.0000    51
H(C11C12C13)
FMATRX   52   2  52  52  17- 18- 34   0  0  0  0  0  0  1.0000    52
H(C11C12C24)
FMATRX   53   2  53  53  17- 21- 25   0  0  0  0  0  0  1.0000    53
H(C11C15C19)
FMATRX   54   2  54  54  17-  5- 20   0  0  0  0  0  0  1.0000    54
H(C11NC_C14)
FMATRX   55   2  55  55   1-  5- 17   0  0  0  0  0  0  1.0000    55
H(C11NC_FE_)
FMATRX   56   2  56  56  18- 17- 21   0  0  0  0  0  0  1.0000    56
H(C12C11C15)
FMATRX   57   2  57  57   5- 17- 18   0  0  0  0  0  0  1.0000    57
H(C12C11NC_)
FMATRX   58   2  58  58  18- 19- 20   0  0  0  0  0  0  1.0000    58
H(C12C13C14)
FMATRX   59   2  59  59  18- 19- 36   0  0  0  0  0  0  1.0000    59
H(C12C13C26)
FMATRX   60   2  60  60  19- 18- 34   0  0  0  0  0  0  1.0000    60
H(C13C12C24)
FMATRX   61   2  61  61   5- 20- 19   0  0  0  0  0  0  1.0000    61
H(C13C14NC_)
FMATRX   62   2  62  62  12- 16- 20   0  0  0  0  0  0  1.0000    62
H(C14C10C6_)
FMATRX   63   2  63  63  20- 19- 36   0  0  0  0  0  0  1.0000    63
H(C14C13C26)
FMATRX   64   2  64  64   1-  5- 20   0  0  0  0  0  0  1.0000    64
H(C14NC_FE_)
FMATRX   65   2  65  65   5- 17- 21   0  0  0  0  0  0  1.0000    65
H(C15C11NC_)
FMATRX   66   2  66  66  21- 25- 24   0  0  0  0  0  0  1.0000    66
H(C15C19C18)
FMATRX   67   2  67  67   6- 25- 21   0  0  0  0  0  0  1.0000    67
H(C15C19ND_)
FMATRX   68   2  68  68  22- 23- 24   0  0  0  0  0  0  1.0000    68
H(C16C17C18)
FMATRX   69   2  69  69  22- 23- 33   0  0  0  0  0  0  1.0000    69
H(C16C17C23)
FMATRX   70   2  70  70  10- 26- 22   0  0  0  0  0  0  1.0000    70
H(C16C20C4_)
FMATRX   71   2  71  71  22-  6- 25   0  0  0  0  0  0  1.0000    71
H(C16ND_C19)
FMATRX   72   2  72  72   1-  6- 22   0  0  0  0  0  0  1.0000    72
H(C16ND_FE_)
FMATRX   73   2  73  73  23- 22- 26   0  0  0  0  0  0  1.0000    73
H(C17C16C20)
FMATRX   74   2  74  74   6- 22- 23   0  0  0  0  0  0  1.0000    74
H(C17C16ND_)
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FMATRX   75   2  75  75  23- 24- 25   0  0  0  0  0 1.0000    75
H(C17C18C19)
FMATRX   76   2  76  76  23- 24- 35   0  0  0  0  0 1.0000    76
H(C17C18C25)
FMATRX   77   2  77  77  24- 23- 33   0  0  0  0  0 1.0000    77
H(C18C17C23)
FMATRX   78   2  78  78   6- 25- 24   0  0  0  0  0 1.0000    78
H(C18C19ND_)
FMATRX   79   2  79  79  25- 24- 35   0  0  0  0  0 1.0000    79
H(C19C18C25)
FMATRX   80   2  80  80   1-  6- 25   0  0  0  0  0 1.0000    80
H(C19ND_FE_)
FMATRX   81   2  81  81   7-  8- 38   0  0  0  0  0 1.0000    81
H(C1_C2_C28)
FMATRX   82   2  82  82   7-  8-  9   0  0  0  0  0 1.0000    82
H(C1_C2_C3_)
FMATRX   83   2  83  83   7- 11- 15   0  0  0  0  0 1.0000    83
H(C1_C5_C9_)
FMATRX   84   2  84  84   7-  3- 10   0  0  0  0  0 1.0000    84
H(C1_NA_C4_)
FMATRX   85   2  85  85   1-  3-  7   0  0  0  0  0 1.0000    85
H(C1_NA_FE_)
FMATRX   86   2  86  86   6- 22- 26   0  0  0  0  0 1.0000    86
H(C20C16ND_)
FMATRX   87   2  87  87   9- 10- 26   0  0  0  0  0 1.0000    87
H(C20C4_C3_)
FMATRX   88   2  88  88   3- 10- 26   0  0  0  0  0 1.0000    88
H(C20C4_NA_)
FMATRX   89   2  89  89  12- 13- 31   0  0  0  0  0 1.0000    89
H(C21C7_C6_)
FMATRX   90   2  90  90  14- 13- 31   0  0  0  0  0 1.0000    90
H(C21C7_C8_)
FMATRX   91   2  91  91   8-  9- 32   0  0  0  0  0 1.0000    91
H(C22C3_C2_)
FMATRX   92   2  92  92  10-  9- 32   0  0  0  0  0 1.0000    92
H(C22C3_C4_)
FMATRX   93   2  93  93  13- 14- 37   0  0  0  0  0 1.0000    93
H(C27C8_C7_)
FMATRX   94   2  94  94  15- 14- 37   0  0  0  0  0 1.0000    94
H(C27C8_C9_)
FMATRX   95   2  95  95   9-  8- 38   0  0  0  0  0 1.0000    95
H(C28C2_C3_)
FMATRX   96   2  96  96  27-  2- 30   0  0  0  0  0 1.0000    96
H(C29NX_C31)
FMATRX   97   2  97  97   1-  2- 27   0  0  0  0  0 1.0000    97
H(C29NX_FE_)
FMATRX   98   2  98  98  27- 28- 29   0  0  0  0  0 1.0000    98
H(C29NY_C30)
FMATRX   99   2  99  99   8-  7- 11   0  0  0  0  0 1.0000    99
H(C2_C1_C5_)
FMATRX  100   2 100 100   3-  7-  8   0  0  0  0  0 1.0000   100
H(C2_C1_NA_)
FMATRX  101   2 101 101   8-  9- 10   0  0  0  0  0 1.0000   101
H(C2_C3_C4_)
FMATRX  102   2 102 102   2- 30- 29   0  0  0  0  0 1.0000   102
H(C30C31NX_)
FMATRX  103   2 103 103  28- 29- 30   0  0  0  0  0 1.0000   103
H(C31C30NY_)
FMATRX  104   2 104 104   1-  2- 30   0  0  0  0  0 1.0000   104
H(C31NX_FE_)
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FMATRX  105   2 105 105   3- 10-  9   0  0   0   0   0 1.0000   105
H(C3_C4_NA_)
FMATRX  106   2 106 106   1-  3- 10   0  0   0   0   0 1.0000   106
H(C4_NA_FE_)
FMATRX  107   2 107 107   3-  7- 11   0  0   0   0   0 1.0000   107
H(C5_C1_NA_)
FMATRX  108   2 108 108  11- 15- 14   0  0   0   0   0 1.0000   108
H(C5_C9_C8_)
FMATRX  109   2 109 109   4- 15- 11   0  0   0   0   0 1.0000   109
H(C5_C9_NB_)
FMATRX  110   2 110 110  12- 13- 14   0  0   0   0   0 1.0000   110
H(C6_C7_C8_)
FMATRX  111   2 111 111  12-  4- 15   0  0   0   0   0 1.0000   111
H(C6_NB_C9_)
FMATRX  112   2 112 112   1-  4- 12   0  0   0   0   0 1.0000   112
H(C6_NB_FE_)
FMATRX  113   2 113 113   4- 12- 13   0  0   0   0   0 1.0000   113
H(C7_C6_NB_)
FMATRX  114   2 114 114  13- 14- 15   0  0   0   0   0 1.0000   114
H(C7_C8_C9_)
FMATRX  115   2 115 115   4- 15- 14   0  0   0   0   0 1.0000   115
H(C8_C9_NB_)
FMATRX  116   2 116 116   1-  4- 15   0  0   0   0   0 1.0000   116
H(C9_NB_FE_)
FMATRX  117   2 117 117   3-  1-  4   0  0   0   0   0 1.0000   117
H(NA_FE_NB_)
FMATRX  118   2 118 118   3-  1-  6   0  0   0   0   0 1.0000   118
H(NA_FE_ND_)
FMATRX  119   2 119 119   2-  1-  3   0  0   0   0   0 1.0000   119
H(NA_FE_NX_)
FMATRX  120   2 120 120   4-  1-  5   0  0   0   0   0 1.0000   120
H(NB_FE_NC_)
FMATRX  121   2 121 121   2-  1-  4   0  0   0   0   0 1.0000   121
H(NB_FE_NX_)
FMATRX  122   2 122 122   5-  1-  6   0  0   0   0   0 1.0000   122
H(NC_FE_ND_)
FMATRX  123   2 123 123   2-  1-  5   0  0   0   0   0 1.0000   123
H(NC_FE_NX_)
FMATRX  124   2 124 124   2-  1-  6   0  0   0   0   0 1.0000   124
H(ND_FE_NX_)
FMATRX  125   2 125 125   2- 27- 28   0  0   0   0   0 1.0000   125
H(NX_C29NY_)
BEGINOBSFREQS
  1 Isotope 125 labels
                          Na__

  1 Mode001.........    1    0
  2 Mode002.........    2    0
  3 Mode003.........    3    0
  4 Mode004.........    4    0
  5 Mode005.........    5    0
  6 Mode006.........    6    0
  7 Mode007.........    7    0
  8 Mode008.........    8    0
  9 Mode009.........    9    0
 10 Mode010.........   10    0
 11 Mode011.........   11    0
 12 Mode012.........   12    0
 13 Mode013.........   13    0
 14 Mode014.........   14    0
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15	Mode015.....	15	0
16	Mode016.....	16	0
17	Mode017.....	17	0
18	Mode018.....	18	0
19	Mode019.....	19	0
20	Mode020.....	20	0
21	Mode021.....	21	0
22	Mode022.....	22	0
23	Mode023.....	23	0
24	Mode024.....	24	0
25	Mode025.....	25	0
26	Mode026.....	26	0
27	Mode027.....	27	0
28	Mode028.....	28	0
29	Mode029.....	29	0
30	Mode030.....	30	0
31	Mode031.....	31	0
32	Mode032.....	32	0
33	Mode033.....	33	0
34	Mode034.....	34	0
35	Mode035.....	35	0
36	Mode036.....	36	0
37	Mode037.....	37	0
38	Mode038.....	38	0
39	Mode039.....	39	0
40	Mode040.....	40	0
41	Mode041.....	41	0
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72	Mode072.....	72	0
73	Mode073.....	73	0
74	Mode074.....	74	0

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 119 Mode119..... 119    0
 120 Mode120..... 120    0
 121 Mode121..... 121    0
 122 Mode122..... 122    0
 123 Mode123..... 123    0
 124 Mode124..... 124    0
 125 Mode125..... 125    0
ENDOBSFREQS
END
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```
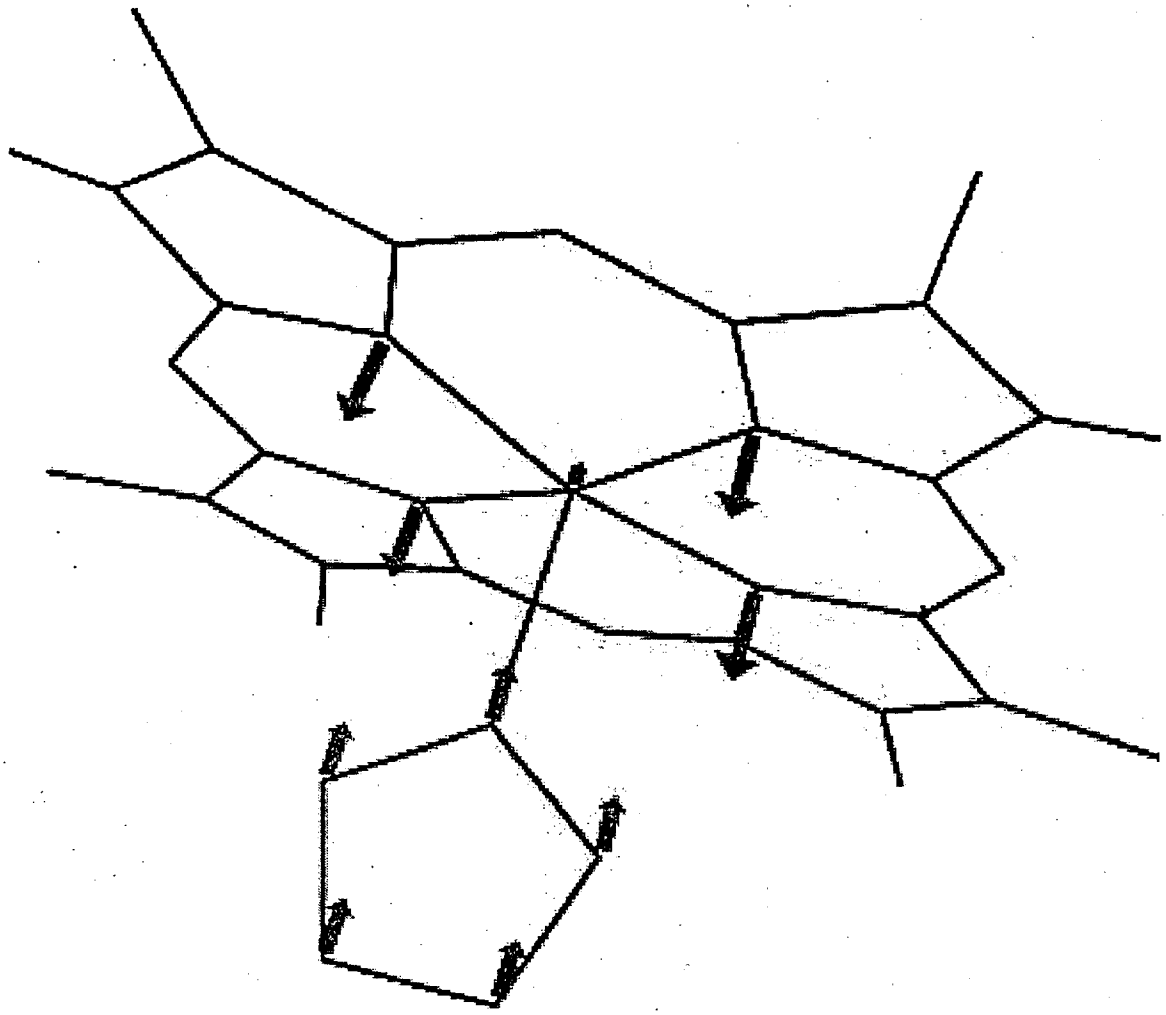
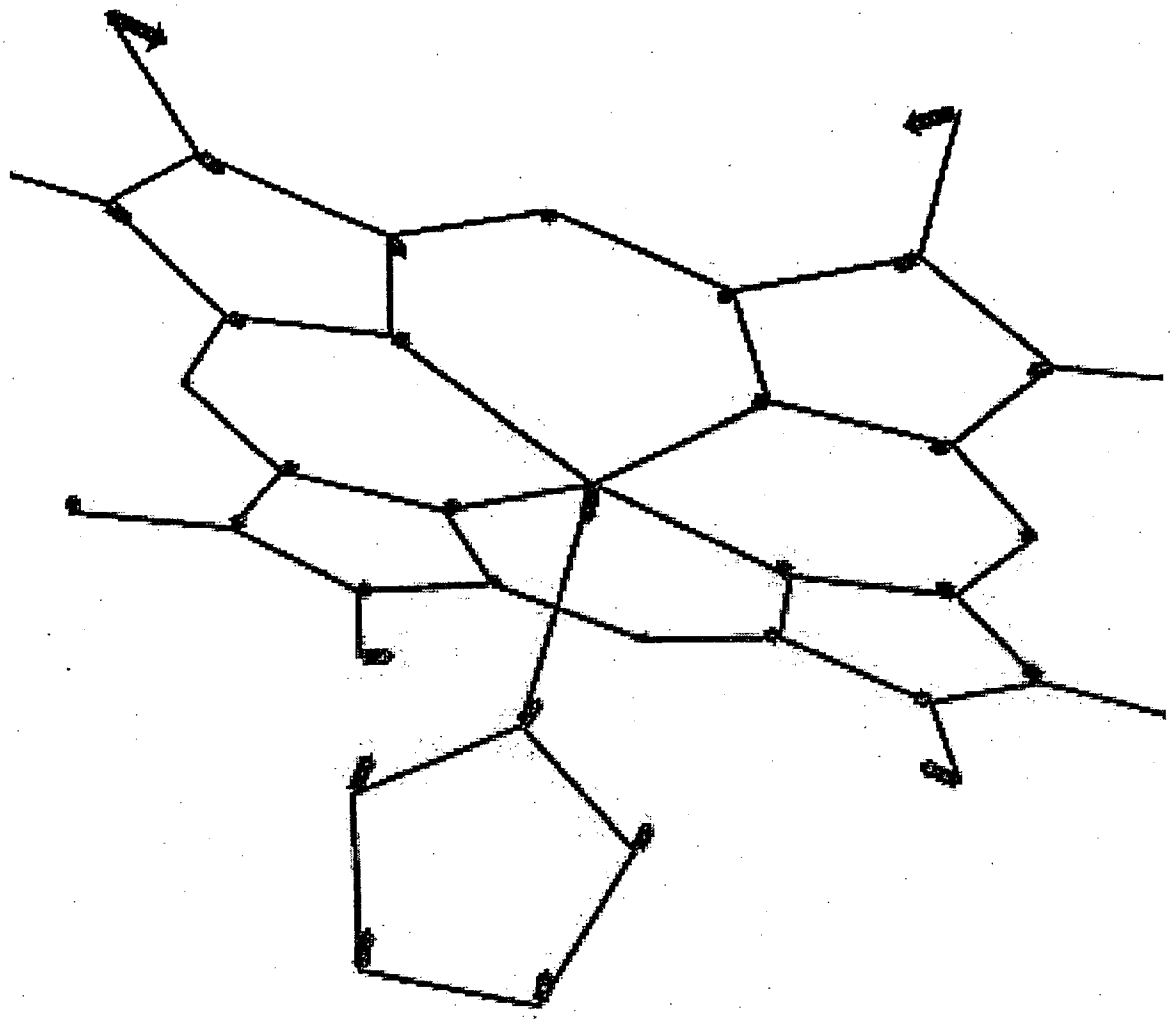

Mode A'' Sombrero 102.4 cm^{-1}

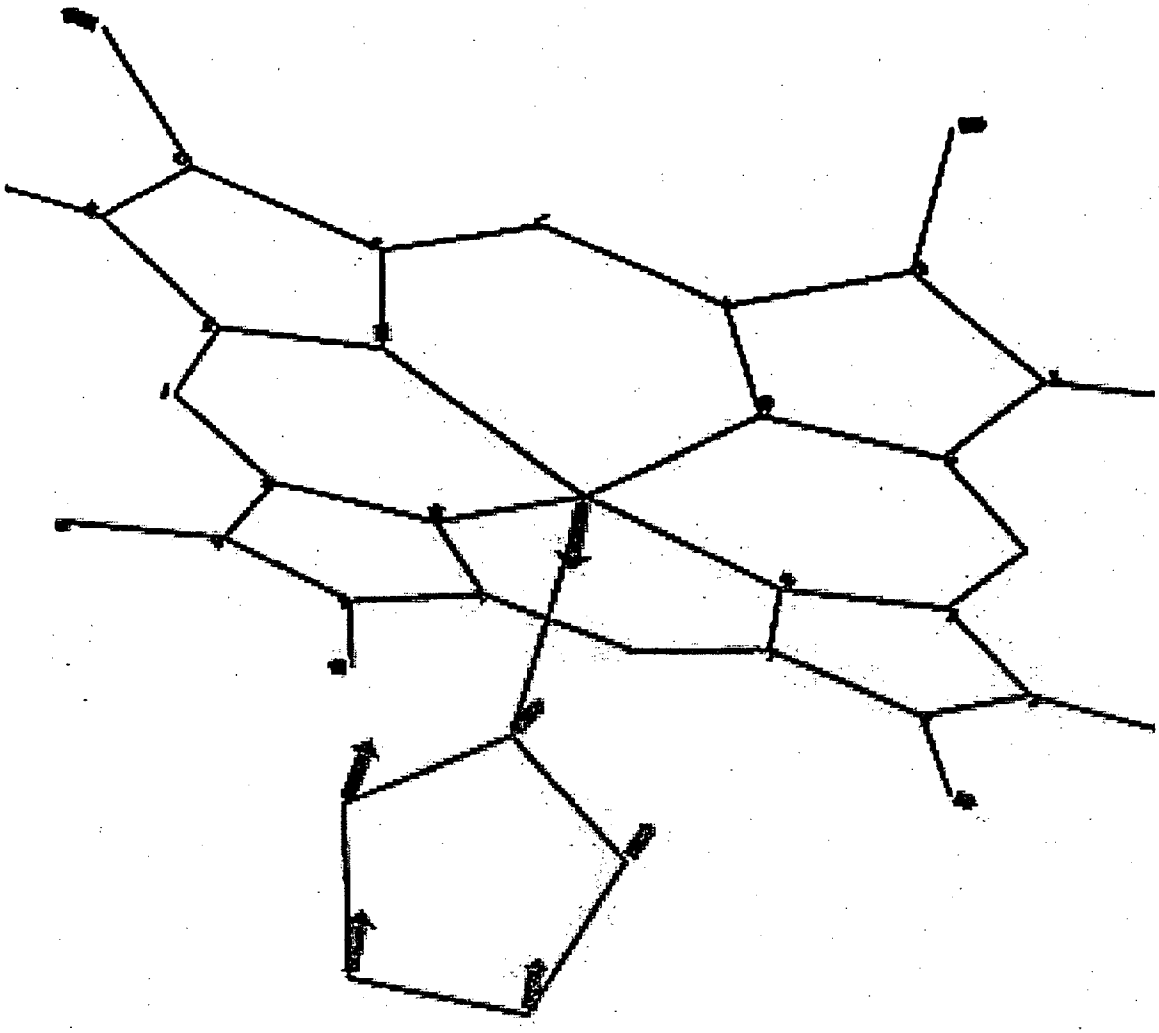
19 % H(ND_FE_NX_)
19 % H(NA_FE_NX_)
18 % H(NC_FE_NX_)
13 % H(NB_FE_NX_)
14 % K(FE_NX)



Mode A' Doming/Breathing 205.7 cm^{-1}
20 % K(FE_NX_)

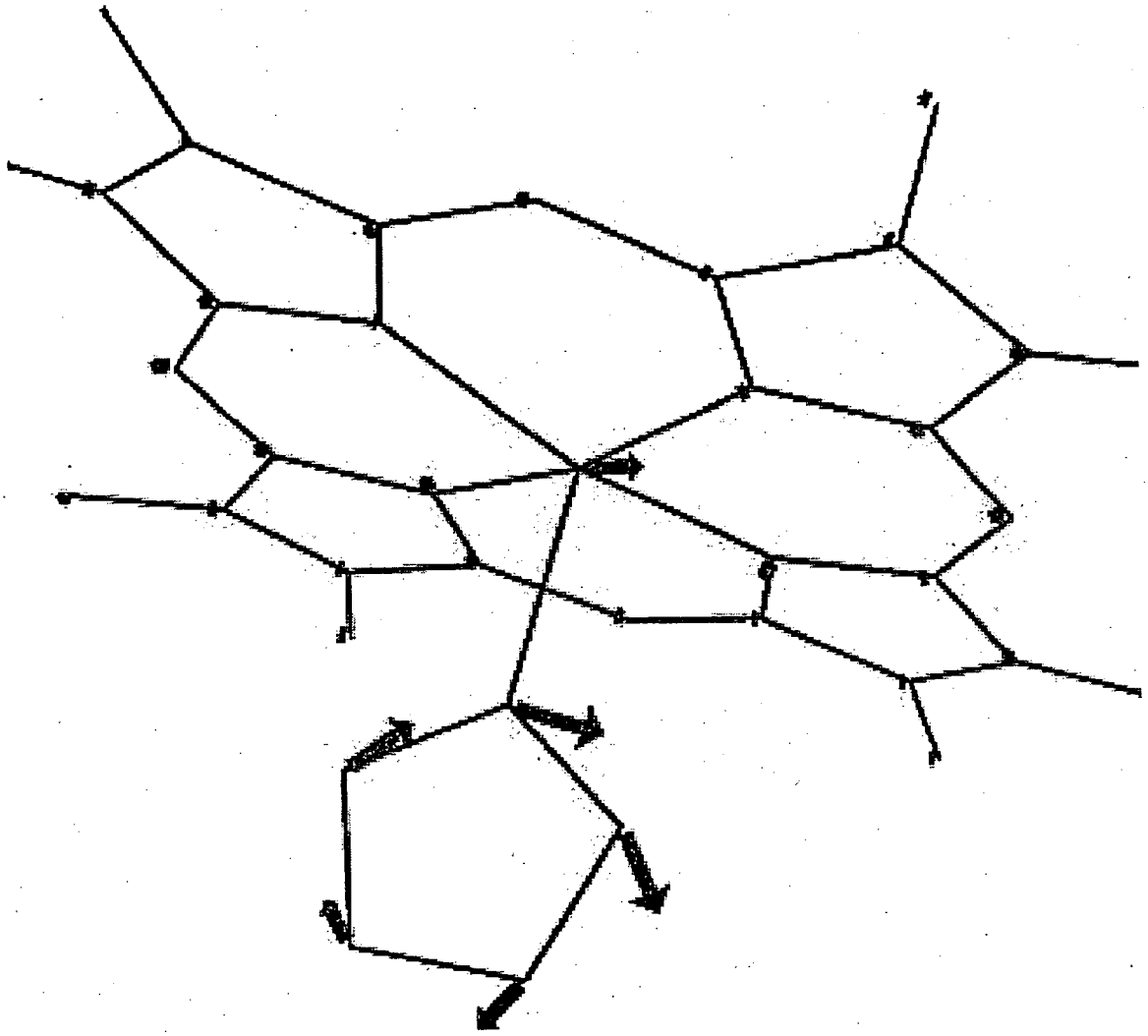


Mode A Doming/Axial Stretching 219.7 cm^{-1}
53 % K(FE_NX_)



Mode B Tilting 229.8 cm^{-1}

```
24 % H(C29NX_FE_)
7  % H(C31NX_FE_)
8  % K(FE_ND_)
8  % K(FE_NA_)
7  % K(FE_NC_)
7  % K(FE_NB_)
```



Fitting Procedure

The fits of the experimental line shape to two Gaussians is illustrated below for both H93G(Im) and H93G(2-Me Im). The fitting function used is a sum of two normalized Gaussians:

$$F(\omega) = \frac{A_1}{\sqrt{2\pi}\sigma_1}\exp\left\{-\frac{(\omega-\omega_1)^2}{2\sigma_1^2}\right\} + \frac{A_2}{\sqrt{2\pi}\sigma_2}\exp\left\{-\frac{(\omega-\omega_2)^2}{2\sigma_2^2}\right\}$$

Table A5. Fits to experimental data in the wavenumber range from 180 - 250 cm^{-1}. A two Gaussian model was used to fit the data.

Ligand	A_1	ω_1	σ_1	A_2	ω_2	σ_2
Im	7560.01	223.533	6.18485	28702.7	227.662	14.4517
d3-Im	7016.74	222.562	6.01776	29509.4	226.495	14.4745
2-Me Im	145366	215.856	11.5496	36045.3	238.416	12.7852
d5 2-Me Im	117985	210.207	10.9328	60419	233.362	13.2352

The fits to two gaussians demonstrate the problem identified in the manuscript that the shift in frequency for the H93G(Im) substitution is too small compared to that expected for a two body model, while that for H93G(2-Me Im) is too large compared to the same model. The fits are illustrated below.

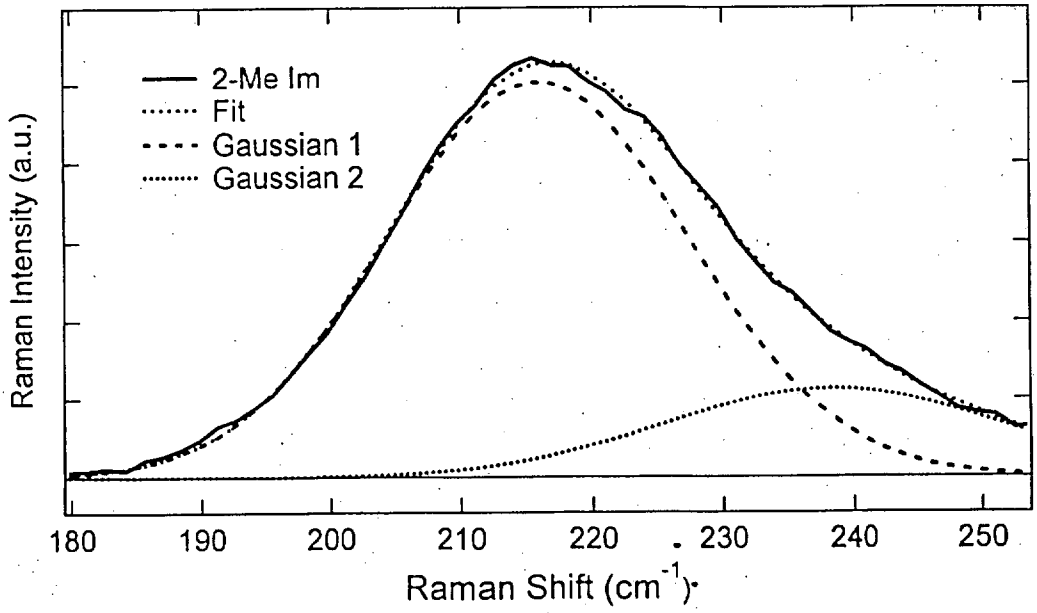


Figure A1. Fit of the data for H93G(2-Me Im) to two Gaussians. Both the fit to the data and individual gaussian components are shown.

The fits do not change qualitatively for the perdeutero isotopomer of 2-methyl imidazole as shown below in Figure A2.

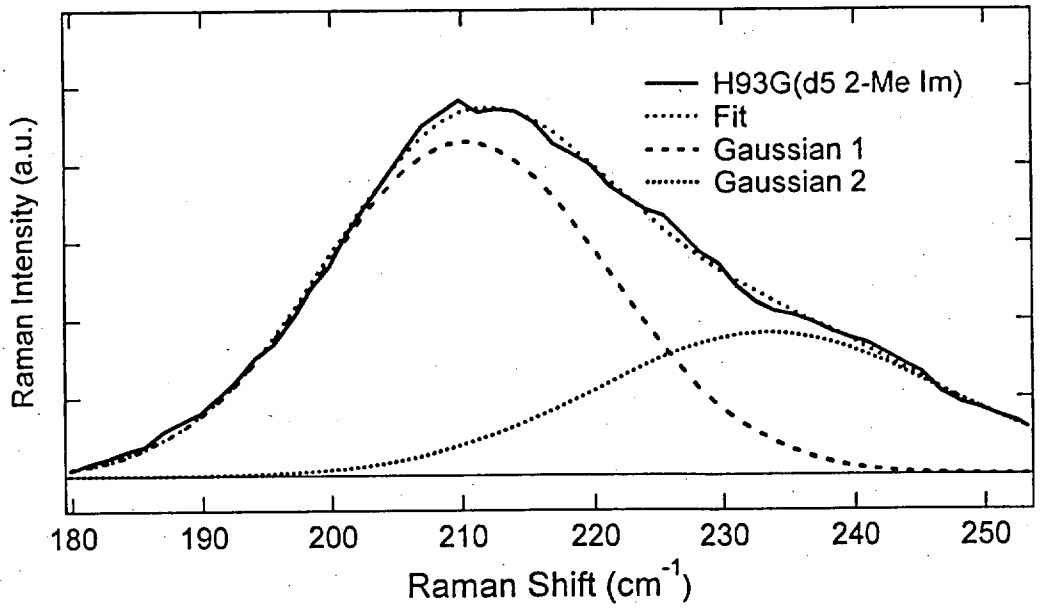


Figure A2. Fit of the axial-ligand out-of-plane band of H93G(d5 2-Me Im) to a two Gaussian model.

A similar situation applies for the fits to H93G(Im) and the d3 isotopomer as shown in Figures A3 and A4 below.

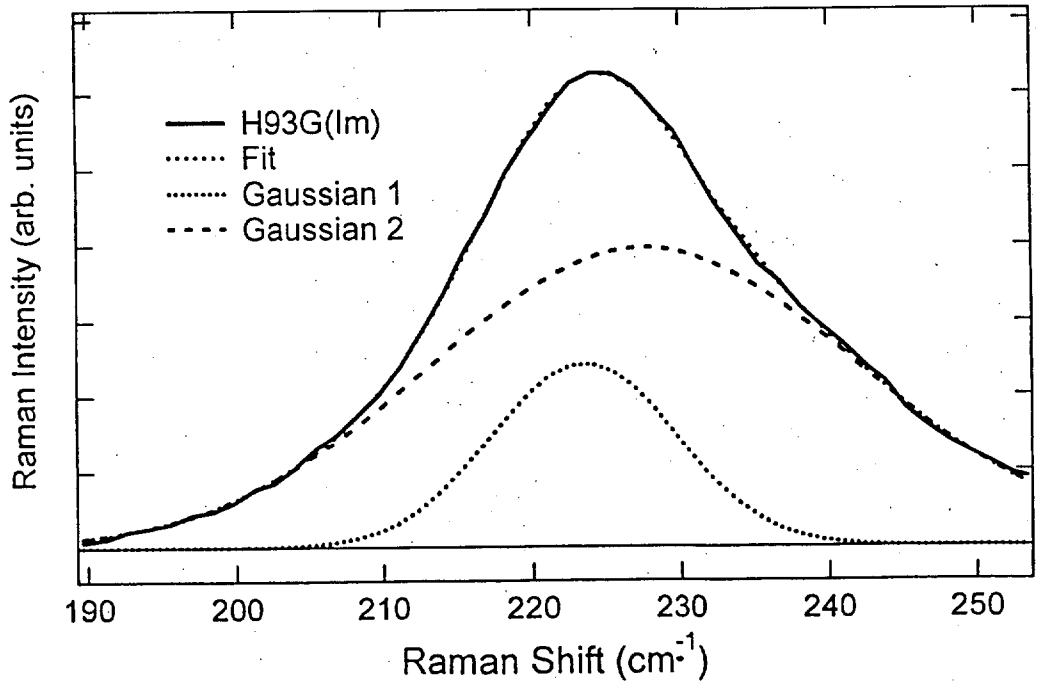


Figure A3. The fit to the axial-ligand out-of-plane band for the imidazole adduct of H93G to a two Gaussian model. Note that the extremely broad peak centered at ca.

227 cm^{-1} does not have a physical interpretation, however, the shift in that peak is within 0.2 cm^{-1} of the magnitude of the smaller peak in the data for the d3-Im isotopomer (Figure A4).

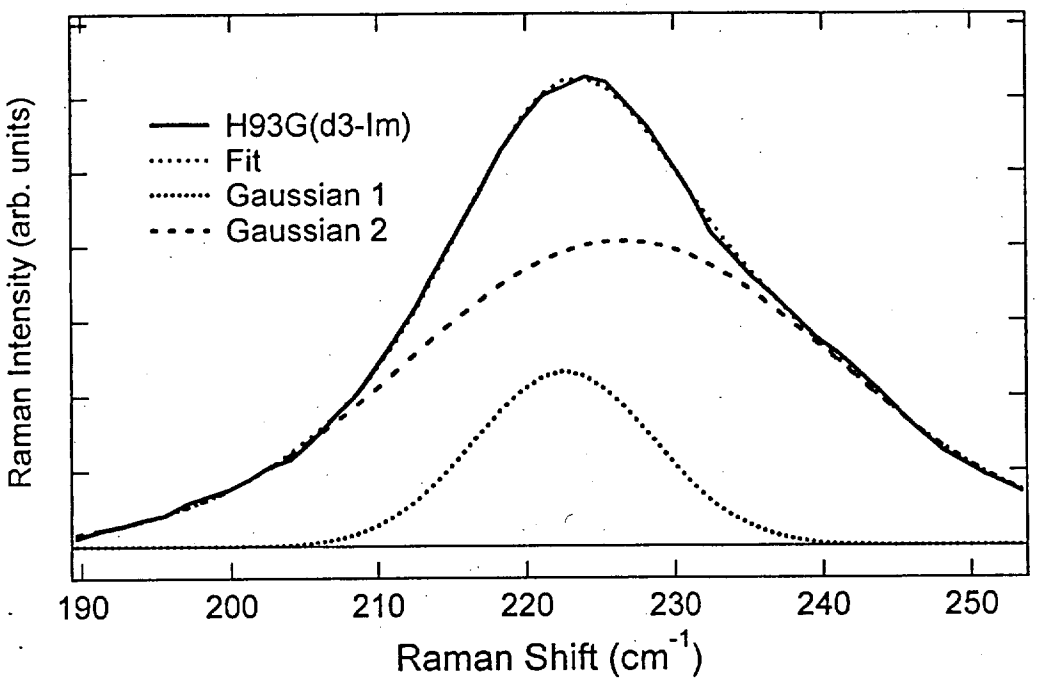


Figure A4. The fit of the axial-ligand out-of-plane band for H93G(d3 Im) to a two Gaussian model.

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