Local Vibrational Modes: A new Tool to Describe the Electronic Structure of Molecules

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How to use computational methods

for increasing the power of

experimental methods ?

Design of CalEx methods

Calculational “Grafting” of Experimental Data

Precise description of electronic structure and bonding

with experimental means

Tools

X-ray	NMR	MS	VibSpec	UV	PES
ED			IR		UPS
MW			Raman		XPS
					Auger

geometry	shifts SSCC	fragm. pattern	bond strength charge distribution	excited states	IPs EAs

How to connect to bond strength and electronic structure?

Modern Vibrational Spectroscopy → High Performance Vibrational Spectroscopy

Inrared

Near IR and Far IR

Fourier transform IR (FTIR)

Two-dimensional IR

Nonlinear 2D IR

Transmission IR

Diffuse Reflectance IR Spect. (DRIFTS)

Reflection-Absorption IR Spectr. (RAIRS)

Multiple Internal Reflection Spectr.

Raman

Fourier transform Raman

Raman Optical Active Spectr. (ROA)

Femtosecond Stimulated Raman Spect.

Coherent anti-Stokes Raman Spectroscopy (CARS)

Resonance Raman Spectroscopy

Surface Enhanced Raman Spectr. (SERS)

Tip Enhanced Raman Spectr. (TERS)

Vibrational Spectroscopy

as a generally applicable

tool for the description of

Chemical Bonding

Molecular vibrations probe the strength of chemical bonds.

Vibrational frequency and vibrational force constant of a stretching vibration can be related to the bond strength, i.e. to the Intrinsic Bond Dissociation Energy (IBDE) of a bond.

Normal vibrational modes

are always delocalized

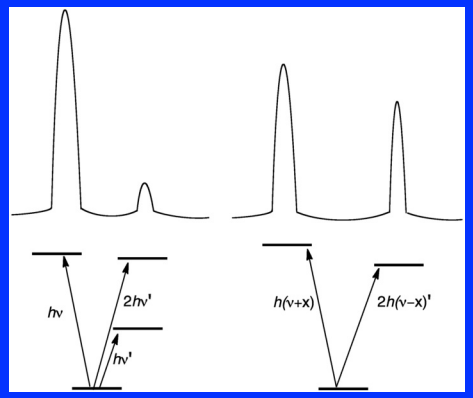
Individual bond stretching modes

cannot be identified!

Normal vibrational modes are always delocalized

because of

Mode-mode coupling



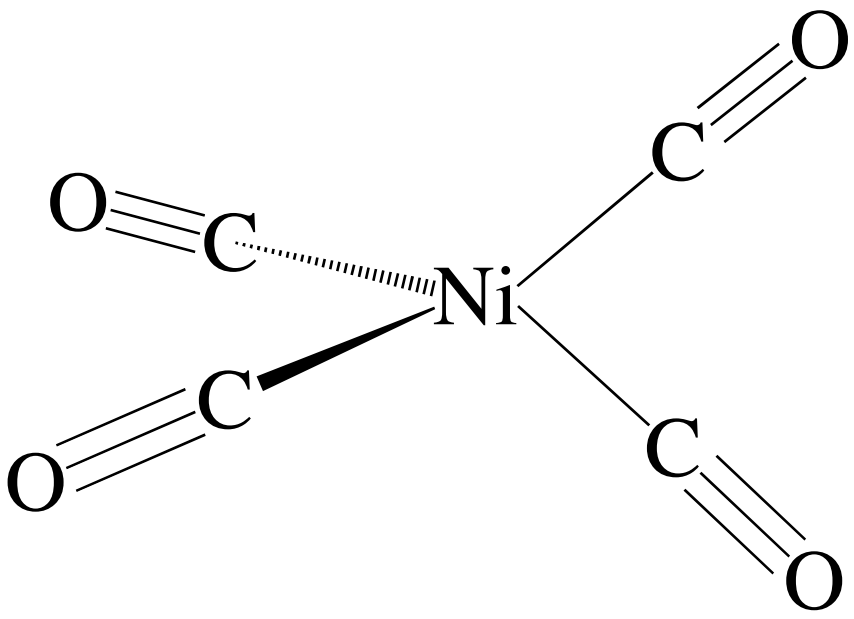
i) electronic coupling: non-diagonal force constants

ii) mass coupling: depends on ratio of masses, direction of mode vectors; closeness of eigen values

Fermi resonances

Closeness of frequency and overtone identical symmetries

Nickeltetracarbonyl

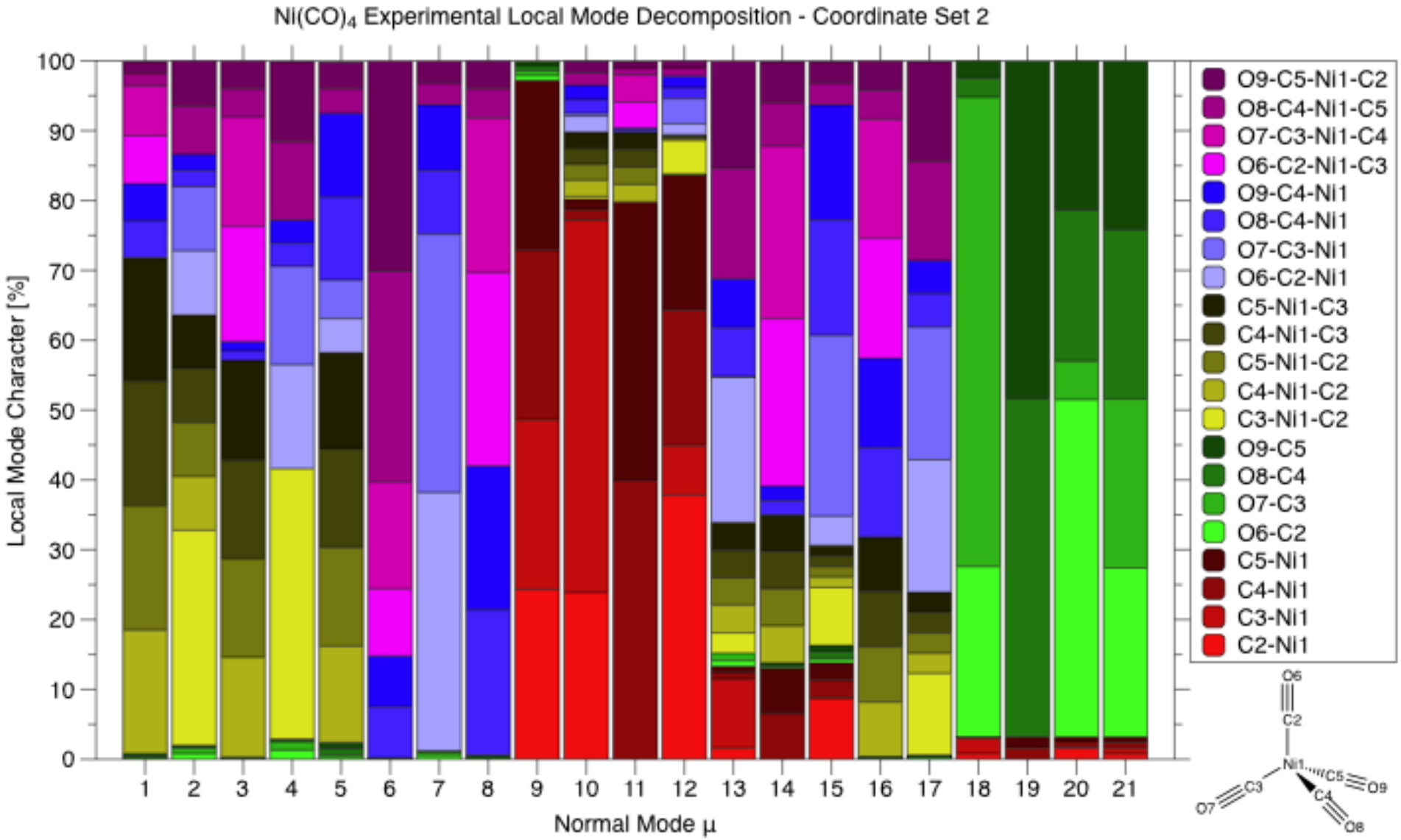


9 atoms ⟶ 3 x 9 - 6 = 21 modes

8 stretches

5 + 4 x 2 bends

Normal vibrational modes of $Ni(CO)_4$: Exp. frequencies



Normal mode vibrations are decomposed into local modes

Local Vibrational Modes

Adiabatic Internal Coordinate Modes: AICoMs

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Relating normal vibrational modes to local vibrational modes with the help of an adiabatic connection scheme

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Information on the electronic structure of a molecule and its chemical bonds is encoded in the molecular normal vibrational modes. However, normal vibrational modes result from a coupling of local vibrational modes, which means that only the latter can provide detailed insight into bonding and other structural features. In this work, it is proven that the adiabatic internal coordinate vibrational modes of Konkoli and Cremer [Int. J. Quantum Chem. **67**, 29 (1998)] represent a unique set of local modes that is directly related to the normal vibrational modes. The missing link between these two sets of modes are the compliance constants of Decius, which turn out to be the reciprocals of the local mode force constants of Konkoli and Cremer. Using the compliance constants matrix, the local mode frequencies of any molecule can be converted into its normal mode frequencies with the help of an adiabatic connection scheme that defines the coupling of the local modes in terms of coupling frequencies and reveals how avoided crossings between the local modes lead to changes in the character of the normal modes. [http://dx.doi.org/10.1063/1.4747339]

- The local vibrational modes are the true equivalent of the normal vibrational modes.

- For a given set of internal coordinates, there is only one set of local modes, which is directly related to the normal vibrational modes.

How to get the normal vibrational modes?

Solving the Euler-Lagrange Equations (I)

$$\frac{d}{dt}\frac{\partial L(\mathbf{x},\dot{\mathbf{x}})}{\partial \dot{x}_i} - \frac{\partial L(\mathbf{x},\dot{\mathbf{x}})}{\partial x_i} = 0 \quad i = 1, \cdots, 3N$$

where $\mathbf{x}$ is a displacement vector expressed in Cartesian coordinates

$$L(\mathbf{x},\dot{\mathbf{x}}) = T(\dot{\mathbf{x}}) - V(\mathbf{x}) \qquad \textit{Lagrangian}$$

$$T(\dot{\mathbf{x}}) = \frac{1}{2}\dot{\mathbf{x}}^{\dagger}\mathbf{M}\dot{\mathbf{x}}$$

$\mathbf{M}$: mass matrix with atom masses m_i

$$V(\mathbf{x}) = \frac{1}{2}\dot{\mathbf{x}}^{\dagger}\mathbf{f}^{x}\dot{\mathbf{x}}$$

The solutions lead to the normal mode vectors $\mathbf{l}_\mu$ and the corresponding normal coordinates Q_μ according to

$$\mathbf{x} = \mathbf{l}_\mu Q_\mu$$

where Q_μ oscillates with the frequency ω_μ.

$\mathbf{f^x L = ML\Lambda}$ **Vibrational Eigenvalue Problem (Cartesian space)**

where $\mathbf{f^x}$ is the force constant matrix, $\mathbf{L}$ collects the vibrational eigenvectors $\mathbf{l}_\mu$ and $\mathbf{M}$ is the mass matrix of the molecule in question.

$$\textit{Vibrational eigenvalues}: \quad \lambda_\mu = 4\pi^2 c^2 \omega_\mu^2$$

Solving the Euler-Lagrange Equations (II)

The Euler-Lagrange equations can also be expressed in internal coordinates q_m:

$$p_m = \frac{\partial L(\mathbf{q}, \dot{\mathbf{q}})}{\partial \dot{q}_m}$$

$$\frac{d}{dt} p_m = \frac{\partial L(\mathbf{q}, \dot{\mathbf{q}})}{\partial q_m} \qquad for \quad m = 1, \cdots, N_{para}$$

for N_{para} being the number of internal coordinates, which we specify for reasons of simplicity to be $N_{para} = N_{vib}$.

$$L(\mathbf{q}, \dot{\mathbf{q}}) = \frac{1}{2} \dot{\mathbf{q}}^{\dagger} \mathbf{G}^{-1} \dot{\mathbf{q}} - \frac{1}{2} \mathbf{q}^{\dagger} \mathbf{F}^{q} \mathbf{q}$$

where matrix $\mathbf{G}$ is the Wilson G-Matrix.

$\mathbf{F^q D = G^{-1} D \Lambda}$ **Wilson Equation**

Basic Equations of Vibrational Spectroscopy

Cartesian Coordinate Space

$\mathbf{f}^x \mathbf{l}_\mu = \lambda_\mu \mathbf{M} \mathbf{l}_\mu$

$\lambda_\mu = 4\pi^2 c^2 \omega_\mu^2$

$\mathbf{f}^x$: Force constant matrix

$\mathbf{M}$: Mass matrix

$\mathbf{l}_\mu$: Normal mode vector

$\mathbf{f}^x \mathbf{L} = \mathbf{M} \mathbf{L} \Lambda$

Internal Coordinate Space

$\mathbf{F}^q \mathbf{d}_\mu = \lambda_\mu \mathbf{G}^{-1} \mathbf{d}_\mu$

$F^q_{nm} = \mathbf{c}_n^\dagger \mathbf{f}^x \mathbf{c}_m$

$\mathbf{F}$: Force constant matrix

$\mathbf{G}$: Wilson's G-matrix

$\mathbf{d}_\mu$: Normal mode vector

$\mathbf{F}^q \mathbf{D} = \mathbf{G}^{-1} \mathbf{D} \Lambda$

$\mathbf{l}_\mu = \mathbf{C} \mathbf{d}_\mu$

Matrix **C** transforms the normal mode vector from internal to Cartesian coordinate space.

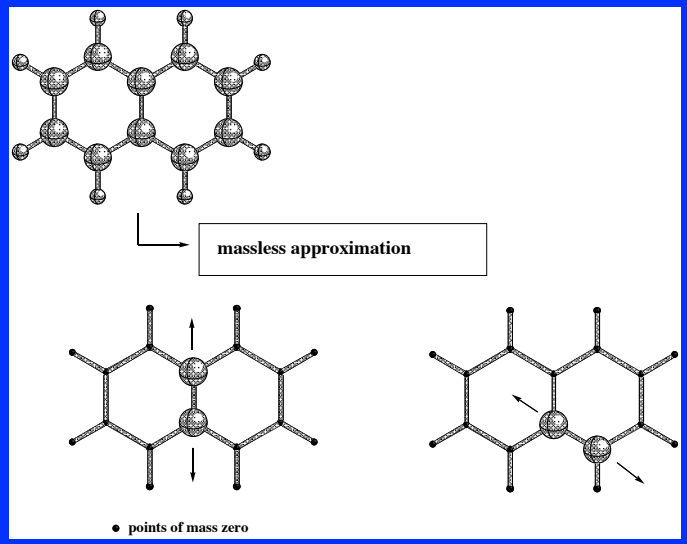
How to get the Local Modes?

Diagonalization of force constant matrix: suppression of electronic coupling

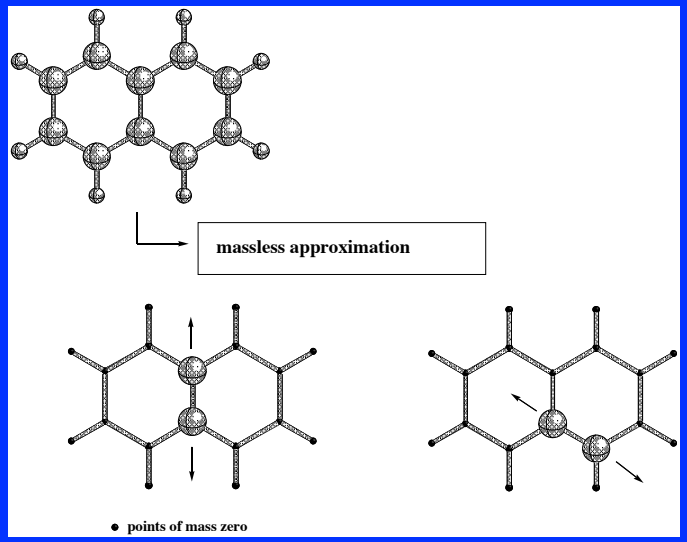
Then, we suppress mass-coupling

Electronic coupling is suppressed by finding the normal mode vectors.
However, kinematic (mass) coupling) cannot be eliminated when obtaining the normal modes.

Mass-Decoupling



Mass-Decoupling



Solution:
Determine the mass-decoupled Euler-Lagrange Equations

The masses of a K_n-atomic molecular fragment are given as m_i, $i = 1, \cdot, 3K_n$. All other masses are set equal to zero, which implies that the corresponding momenta $p_j = 0$.

Equations of motion:

$$\dot{p}_i = \frac{\partial V}{\partial x_i} \quad for \;\; i = 1, \cdots, 3K_n$$

$$0 = \frac{\partial V}{\partial x_j} \quad for \;\; j = 3K_n + 1, \cdots, 3N$$

with

$$p_i = \frac{\partial L}{\partial \dot{x}_i} = m_i \dot{x}_i \quad for \;\; i = 1, \cdots, 3K_n$$

$$p_j = 0 \quad for \;\; j = 3K_n + 1, \cdots, 3N$$

Solution:

$$\lambda_i = \frac{\partial V}{\partial x_i} \quad for \;\; i = 1, \cdots, 3K_n$$

$$0 = \frac{\partial V}{\partial x_j} \quad for \;\; j = 3K_n + 1, \cdots, 3N$$

Using

$$x_k = x_k(\lambda_i, \cdots, \lambda_{3K_n}) \quad k = 1, \cdots, 3K$$

and the above equations the time dependence of λ_i and x_k can be found

Local Modes in the Harmonic Approximation

Assume that the vibrational problem has been solved, the potential energy V and an internal coordinate $\mathbf{q_n}$

$(x_1, x_2, ..., x_{3Kn}) \longrightarrow q_n$

can be expressed as function of $\mathbf{N_{vib}}$ normal mode coordinates $\mathbf{Q_\mu}$, and the corresponding force constants $\mathbf{k_\mu}$:

$$V(\mathbf{Q}) = \frac{1}{2} \sum_{\mu=1}^{N_{vib}} k_\mu Q_\mu^2 \qquad (1)$$

$$q_n(\mathbf{Q}) = \sum_{\mu=1}^{N_{vib}} D_{n\mu} Q_\mu \qquad (2)$$

Matrix **D** collects the column vectors $\mathbf{d_\mu}$, which represent the normal modes μ in internal coordinate space.

Leading the local mode by q_n^* and relaxing all other internal coordinates q_m (Leading parameter principle):

$$q_n(\mathbf{Q}) = q_n^* \tag{3}$$

$$\frac{\partial}{\partial Q_\mu}\left[V(\mathbf{Q}) - \lambda\left(q_n(\mathbf{Q}) - q_n^*\right)\right] = 0 \tag{4}$$

$$Q_\mu^{(n)} = \frac{D_{n\mu}}{k_\mu}\lambda \tag{5}$$

$$\lambda = \frac{1}{\sum_{\mu=1}^{N_{vib}} \frac{D_{n\mu}^2}{k_\mu}} q_n^* \tag{6}$$

$$Q_\mu^{(n)} = Q_{\mu n}^0 \; q_n^* \tag{7}$$

The local modes are extracted out of the normal modes expressed in internal coordinates

Elements μ of mode $\mathbf{a}_n$ associated with internal coordinate q_n

$$(\mathbf{a}_n)_\mu = \frac{\frac{D_{n\mu}}{k_\mu}}{\sum_{\nu=1}^{N_{vib}} \frac{D_{n\nu}^2}{k_\nu}} \longrightarrow \mathbf{a}_n^{\mathbf{Q}}$$

$D_{n\mu}$ contribution of displacement q_n to normal mode μ

k_μ force constant of normal mode μ

$N_{vib} = 3N - 6$

Properties of Local Vibrational Modes

Local Mode Vectors

$$\mathbf{a}_n = \frac{\mathbf{K}^{-1}\mathbf{d}_n^\dagger}{\mathbf{d}_n\mathbf{K}^{-1}\mathbf{d}_n^\dagger}$$

Local Mode Force Constant

$$k_a^{(n)} = \mathbf{a}_n^\dagger \mathbf{K} \mathbf{a}_n = (\mathbf{d}_n\mathbf{K}^{-1}\mathbf{d}_n^\dagger)^{-1}$$

Local Mode Mass

$$m_n = (\mathbf{b}_n^\dagger \mathbf{M}^{-1}\mathbf{b}_n)^{-1} = G_{nn}^{-1}$$

Local Mode Frequency

$$4\pi^2 c^2 (\omega_a^{(n)})^2 = k_a^{(n)} G_{nn}$$

Local Mode Intensity

$K = L^\dagger f^x L$

AICoMs
adiabatic
internal
coordinate
modes

Compliance Constants

Derived from the inverse of the force constant matrix

Decius, 1953, 1963

Compliance Constants

Potential energy V expressed in terms of generalized displacement forces (rather than displacements

$$V(\mathbf{g}) = \frac{1}{2}\,\mathbf{g}^{\dagger}\,\mathbf{C}\,\mathbf{g} \qquad \text{rather than} \qquad V(\mathbf{q}) = \frac{1}{2}\,\mathbf{q}^{\dagger}\,\mathbf{F}\,\mathbf{q}$$

$\mathbf{g} = \mathbf{F}\,\mathbf{q}$

$\mathbf{q} = \mathbf{F}^{-1}\,\mathbf{g} = \mathbf{C}\,\mathbf{g}$

q vector of displacement coordinates

g vector of displacement forces

F force constant matrix

C compliance matrix $\qquad \Gamma = \mathbf{C} = \mathbf{F}^{-1}$

C_{ii}: displacement of internal coordinate q_i under the impact of a unit force with all other forces are being relaxed (C_{ij} largely reduced)

Large (small) displacement **weak (strong) bond**

Decius, 1953, 1963

Compliance constants are not useful + are rarely used

- Calculation is too expensive
- They are often inaccurate
- They cannot be related to a vibrational mode
- They do not lead to a frequency or intensity
- Meaning of the off-diagonal elements ?
- Odd description of bond strength

Local Mode Force Constants and Compliance Constants

$$\mathbf{F^q} = (\mathbf{D}^{-1})^\dagger \mathbf{L}^\dagger \mathbf{f^x} \mathbf{L} \mathbf{D}^{-1} = (\mathbf{D}^{-1})^\dagger \mathbf{K} \mathbf{D}^{-1}$$

$$\mathbf{\Gamma^q} = (\mathbf{F^q})^{-1} = \mathbf{D}\mathbf{K}^{-1}\mathbf{D}^\dagger$$

$$(\mathbf{\Gamma^q})_n = \mathbf{d}_n \mathbf{K}^{-1} \mathbf{d}_n^\dagger$$

$k_a^{(n)} = (\mathbf{d}_n \mathbf{K}^{-1} \mathbf{d}_n^{+})^{-1}$

which proves that

$$k_a^{(n)} = 1/(\mathbf{\Gamma^q})_{nn} = 1/\Gamma_n$$

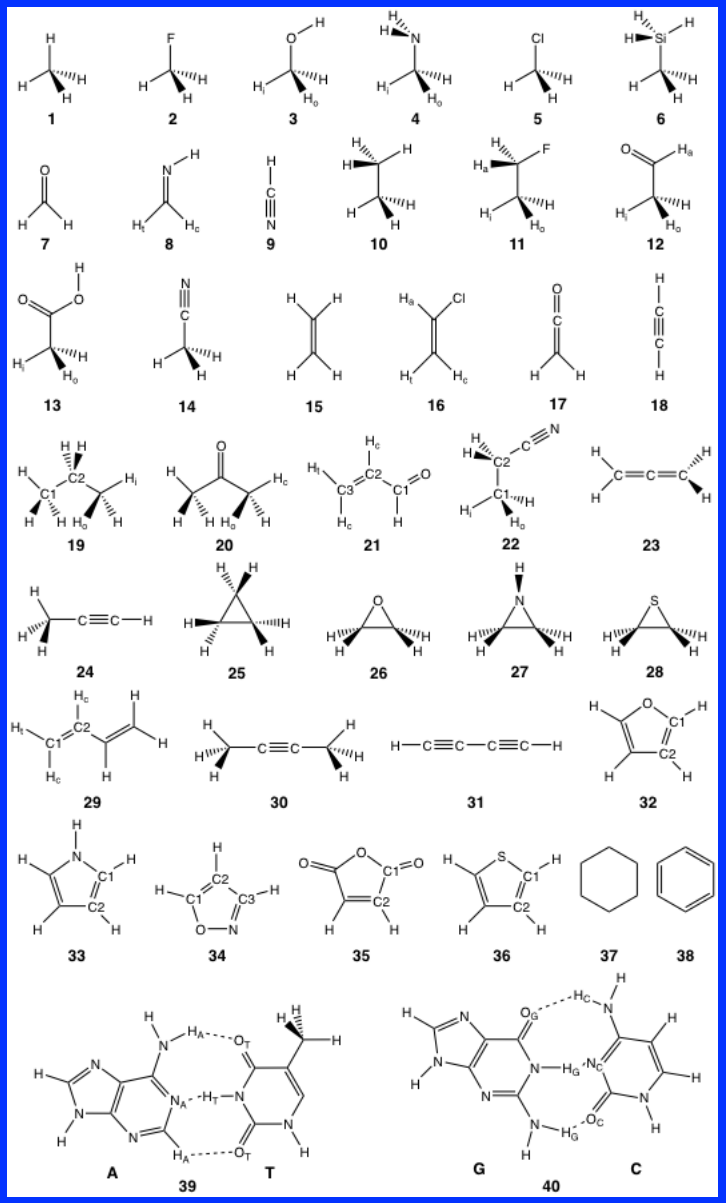
The reciprocal of the compliance constants of Decius are the local mode force constants of Konkoli and Cremer.

$\mathbf{F}^q = \mathbf{C}^\dagger \mathbf{f}^x \mathbf{C}$

$\mathbf{C} = \mathbf{L}\,\mathbf{D}^{-1}$

$\mathbf{K} = \mathbf{L}^\dagger \mathbf{f}^x \mathbf{L}$

W. Zou, R. Kalescky, E. Kraka, and D. Cremer, J. Chem. Phys. 137, 084114 (2012)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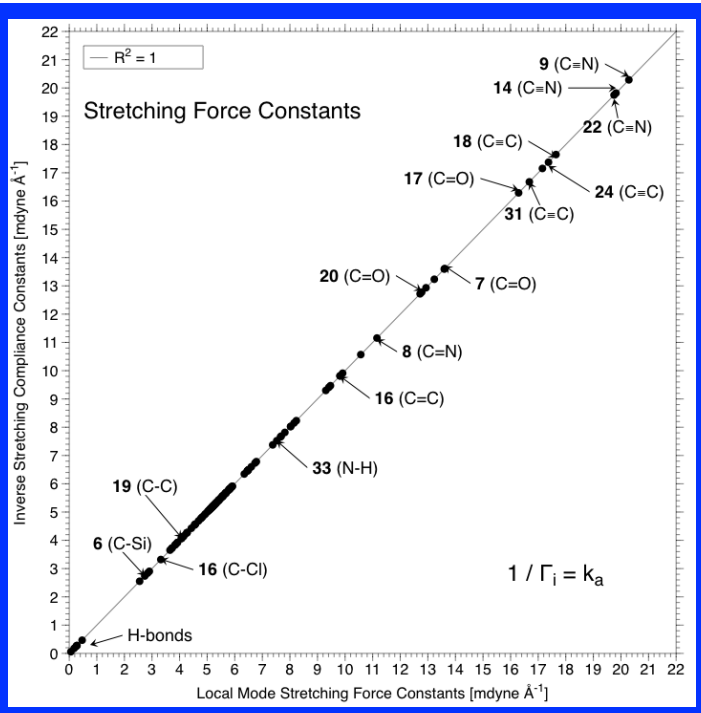
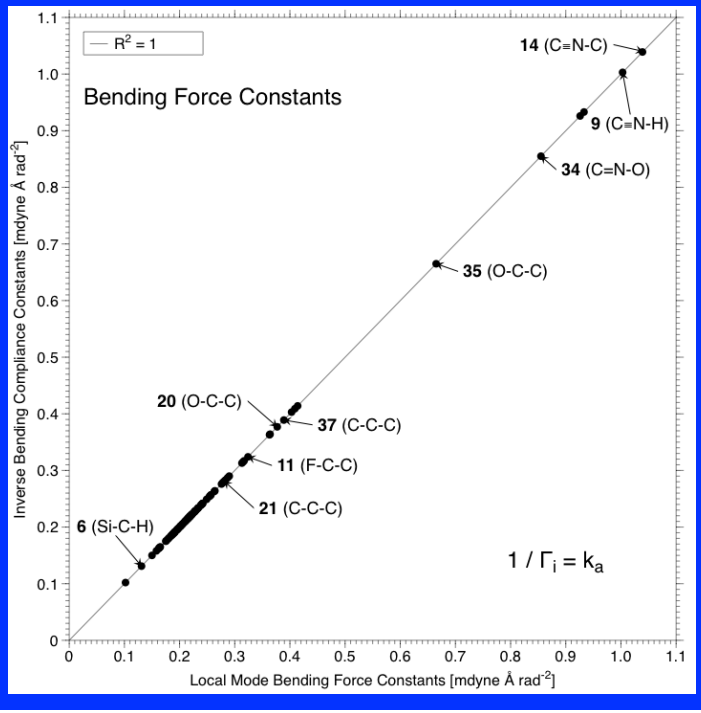
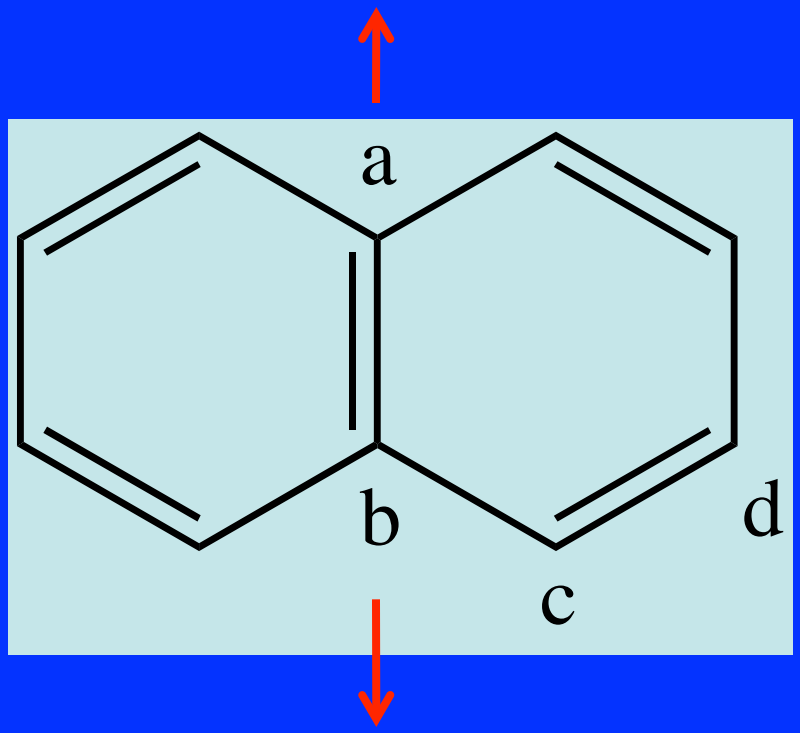

R² = 1
Stretching Force Constants
9 (C≡N)
14 (C≡N)
22 (C≡N)
18 (C≡C)
17 (C=O)
24 (C=C)
31 (C≡C)
20 (C=O)
7 (C=O)
8 (C=N)
16 (C=C)
33 (N-H)
19 (C-C)
6 (C-Si)
16 (C-Cl)
H-bonds
1 / Γi = ka
Inverse Stretching Compliance Constants [mdyne Å-1]
Local Mode Stretching Force Constants [mdyne Å-1]

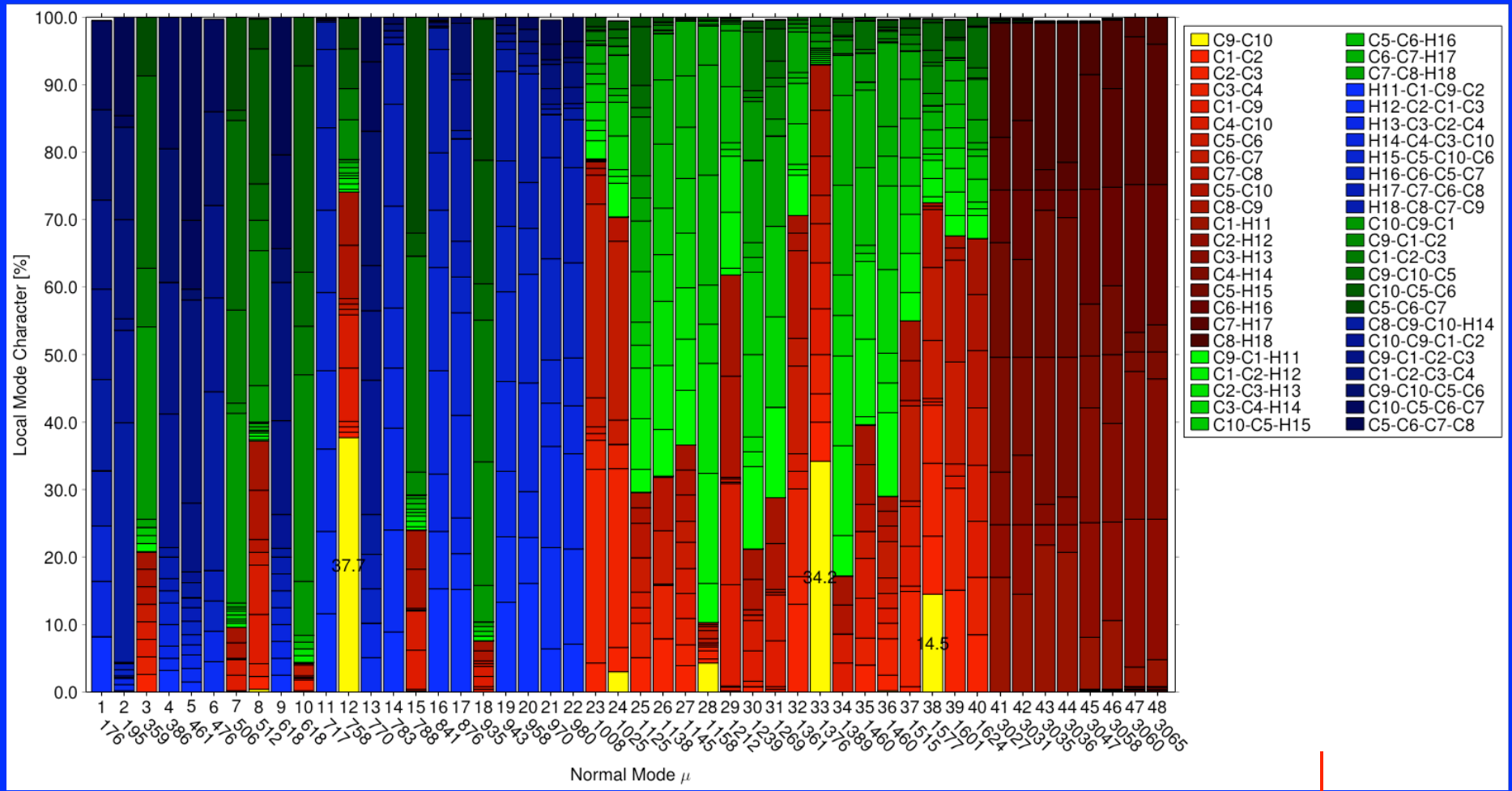

R² = 1
Bending Force Constants
14 (C≡N-C)
9 (C≡N-H)
34 (C=N-O)
35 (O-C-C)
20 (O-C-C)
37 (C-C-C)
11 (F-C-C)
21 (C-C-C)
6 (Si-C-H)
1 / Γi = ka
Inverse Bending Compliance Constants [mdyne Å rad-2]
Local Mode Bending Force Constants [mdyne Å rad-2]

Compliance constants are not useful and superfluous

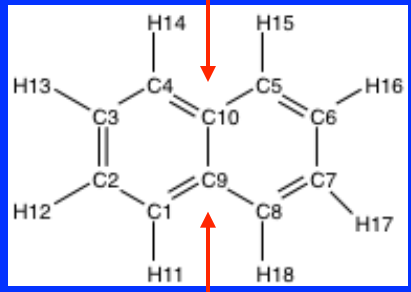
- Calculation is too expensive
- They are often inaccurate
- They cannot be related to a vibrational mode
- They do not lead to a frequency or intensity
- Meaning of the off-diagonal elements ?
- Odd description of bond strength

What are stretching frequency
and force constant of bond a-b of naphthalene?
How do they compare to those of bonds b-c and c-d?

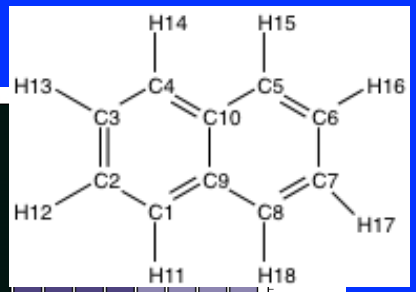




Napthalene: Mode composition given in %



Napthalene



The 48 local modes are pure without any contamination

How to relate local to normal modes ?

Adiabatic Connection Scheme I

$$\mathbf{D}^{\dagger}\mathbf{F}^{q}\mathbf{D} = \mathbf{K} = \mathbf{D}^{\dagger}\mathbf{G}^{-1}\mathbf{D}\mathbf{\Lambda} \qquad \textit{Wilson Equation}$$

$$\mathbf{F}^{a} = \mathbf{A}^{\dagger}\mathbf{K}\mathbf{A} \qquad \textbf{Local Mode Representation of Force Constant Matrix}$$

where $\mathbf{A}$ collects the local mode vectors:

$$\mathbf{A} = \mathbf{K}^{-1}\mathbf{D}^{\dagger}\left[\left(\mathbf{D}\mathbf{K}^{-1}\mathbf{D}^{\dagger}\right)_{d}\right]^{-1}$$

subscript d denotes the diagonal terms of the matrix product

$$\begin{aligned}\mathbf{A}^{\dagger}\mathbf{K}\mathbf{A}(\mathbf{A}^{-1}) = \mathbf{F}^{a}(\mathbf{A}^{-1}) &= (\mathbf{F}^{a}_{d} + \lambda\mathbf{F}^{a}_{o})(\mathbf{A}^{-1}) \\ &= (\mathbf{A}^{\dagger}\mathbf{D}^{\dagger}\mathbf{G}^{-1}\mathbf{D}\mathbf{A})(\mathbf{A}^{-1})\mathbf{\Lambda}\end{aligned}$$

with the diagonal matrix $\mathbf{k}_{a} = \mathbf{F}^{a}_{d}$

Partitioning into a diagonal and an off-diagonal part (as done for the force constant matrix) requires the same for matrix $\mathbf{G}^{-1}$, which is not possible.

Adiabatic Connection Scheme II

The objective can be reached with the help of compliance matrix $\mathbf{\Gamma}^q$

$$(\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{G}^{-1}\mathbf{D}\,\mathbf{\Lambda}$$

$$\mathbf{G}\,(\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{D}\,\mathbf{\Lambda}$$
$$\mathbf{G}[(\mathbf{\Gamma}^q)^{-1}\mathbf{D}] = \mathbf{\Gamma}^q[(\mathbf{\Gamma}^q)^{-1}\mathbf{D}]\mathbf{\Lambda}$$
$$\mathbf{G}\,\mathbf{R} = \mathbf{\Gamma}^q\mathbf{R}\,\mathbf{\Lambda}$$

where a new eigenvector matrix $\mathbf{R}$ is introduced

$$\mathbf{R} = (\mathbf{\Gamma}^q)^{-1}\mathbf{D} = \mathbf{F}^q\mathbf{D} = (\mathbf{D}^{-1})^\dagger\mathbf{K}$$

Adiabatic Connection Scheme

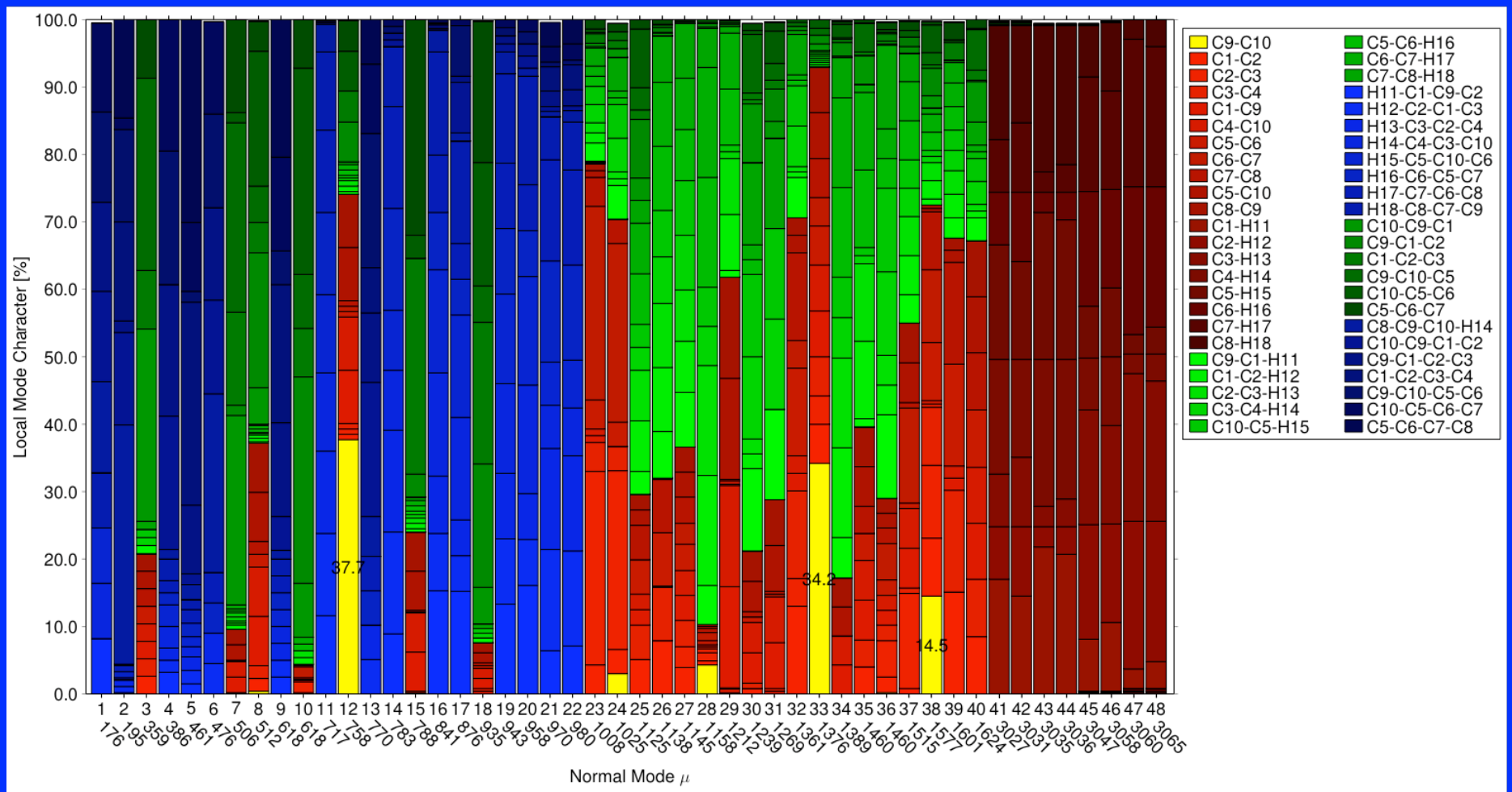
$$(\mathbf{G}_d + \lambda\,\mathbf{G}_o)\,\mathbf{R}_\lambda = (\mathbf{\Gamma}^q_d + \lambda\,\mathbf{\Gamma}^q_o)\,\mathbf{R}_\lambda\mathbf{\Lambda}_\lambda$$

Solution

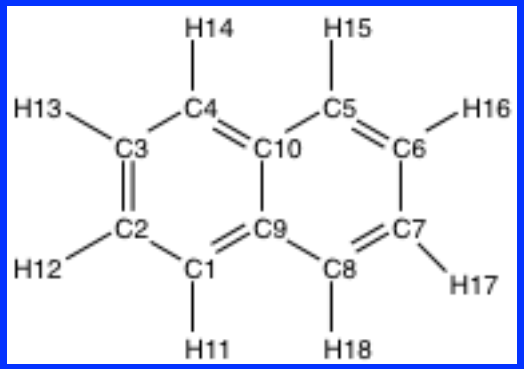
where $\mathbf{R}$ and $\mathbf{\Lambda}$ depend on λ.

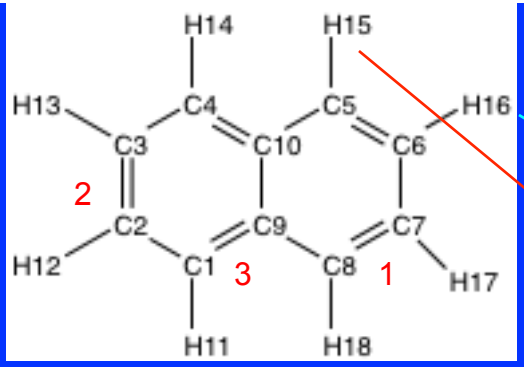
The adiabatic connection scheme relates local to normal vibrational modes in terms of their eigenvalues (frequencies) and eigenvectors (mode vectors).

W. Zou, R. Kalescky, E. Kraka, and D. Cremer, J. Chem. Phys. 137, 084114 (2012)



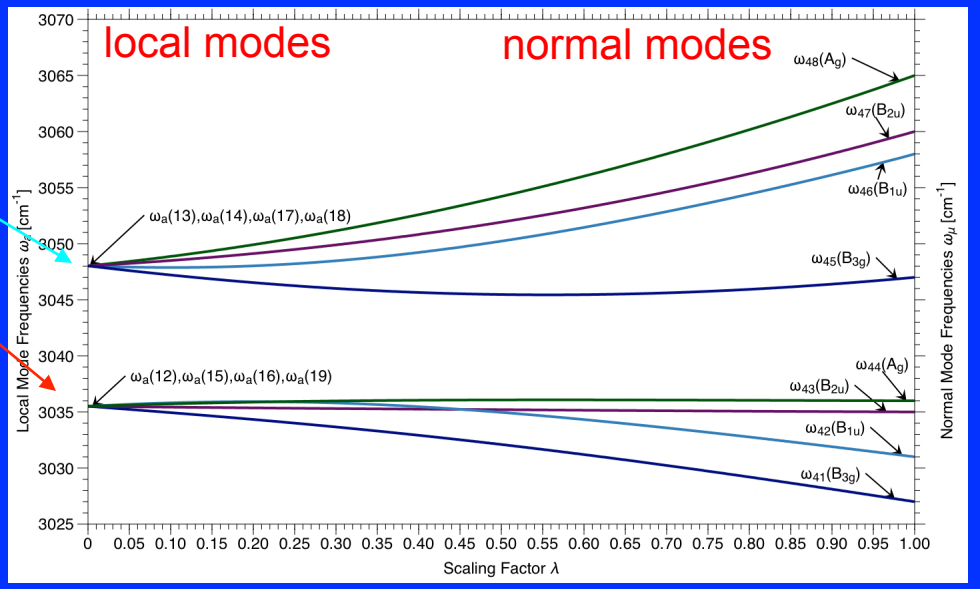
The C9-C10 stretching mode contributes to 5 different modes in the range 750 - 1580 cm^{-1}



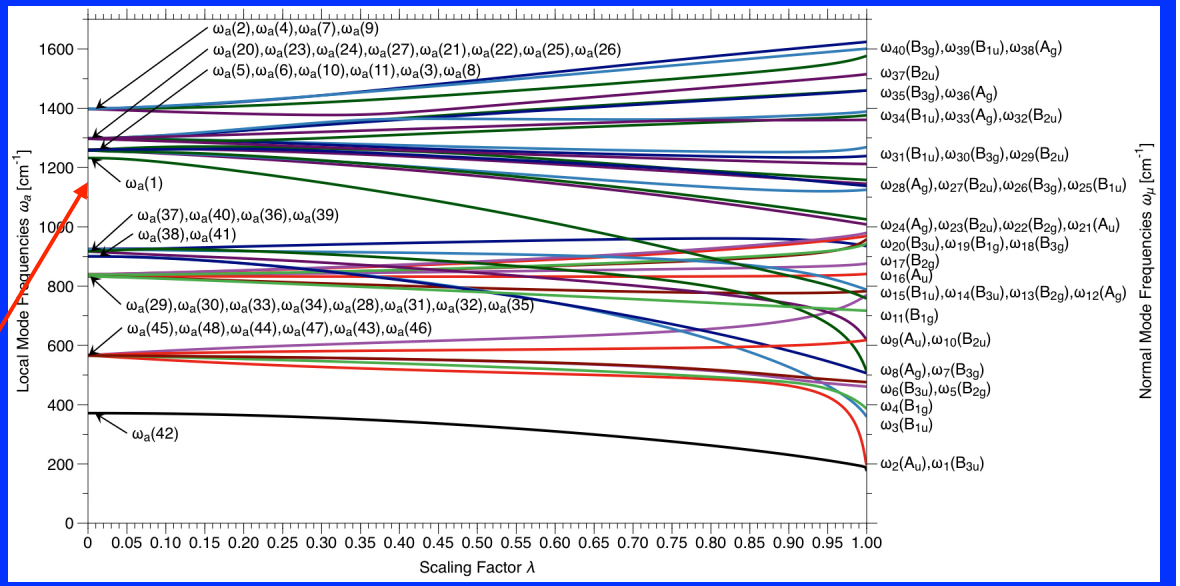


μ	Symm.	ω_μ [cm^{-1}]	Param.	Param. #	k_a [mdyn Å^{-1}]^a	ω_a [cm^{-1}]	ω_{coup} [cm^{-1}]
48	A_g	3065	C2-H12	13	5.089	3048.0	17.0
47	B_{2u}	3060	C3-H13	14	5.089	3048.0	12.0
46	B_{1u}	3058	C6-H16	17	5.089	3048.0	10.0
45	B_{3g}	3047	C7-H17	18	5.089	3048.0	-1.0
44	A_g	3036	C1-H11	12	5.047	3035.5	0.5
43	B_{2u}	3035	C4-H14	15	5.047	3035.5	-0.5
42	B_{1u}	3031	C5-H15	16	5.047	3035.5	-4.5
41	B_{3g}	3027	C8-H18	19	5.047	3035.5	-8.5
40	B_{3g}	1624	C1-C2	2	6.909	1398.0	226.0
39	B_{1u}	1601	C3-C4	4	6.909	1398.0	203.0
38	A_g	1577	C5-C6	7	6.909	1398.0	179.0
37	B_{2u}	1515	C7-C8	9	6.909	1398.0	117.0
35	B_{3g}	1460	C9-C1-H11	20	0.249	1298.2	161.8
36	A_g	1460	C3-C4-H14	23	0.249	1298.2	161.8
34	B_{1u}	1389	C10-C5-H15	24	0.249	1298.2	90.8
33	A_g	1376	C7-C8-H18	27	0.249	1297.3	78.7
32	B_{2u}	1361	C1-C2-H12	21	0.248	1298.2	62.8
31	B_{1u}	1269	C2-C3-H13	22	0.248	1297.3	-28.3
30	B_{3g}	1239	C5-C6-H16	25	0.248	1297.3	-58.3
29	B_{2u}	1212	C6-C7-H17	26	0.248	1297.3	-85.3
28	A_g	1158	C2-C3	3	5.614	1260.2	-102.2
27	B_{2u}	1145	C6-C7	8	5.614	1260.2	-115.2
26	B_{3g}	1138	C1-C9	5	5.595	1258.0	-120.0
25	B_{1u}	1125	C4-C10	6	5.595	1258.0	-133.0
24	A_g	1025	C5-C10	10	5.595	1258.0	-233.0
23	B_{2u}	1008	C8-C9	11	5.595	1258.0	-250.0
22	B_{2g}	980	H12-C2-C1-C3	29	0.298	839.4	140.7
21	A_u	970	H13-C3-C2-C4	30	0.298	839.4	130.7
20	B_{3u}	958	H16-C6-C5-C7	33	0.298	839.4	118.7
19	B_{1g}	943	H17-C7-C6-C8	34	0.298	839.4	103.7
18	B_{3g}	935	C9-C1-C2	37	2.353	925.0	10.1
17	B_{2g}	876	H11-C1-C9-C2	28	0.293	832.6	43.4
16	A_u	841	H14-C4-C3-C10	31	0.293	832.6	8.4
15	B_{1u}	788	C10-C5-C6	40	2.353	925.0	-137.0
14	B_{3u}	783	H15-C5-C10-C6	32	0.293	832.6	-49.6
13	B_{2g}	770	C1-C2-C3-C4	45	0.327	567.5	202.5
12	A_g	758	C9-C10	1	5.368	1232.2	-474.2
11	B_{1g}	717	H18-C8-C7-C9	35	0.293	832.6	-115.6
10	A_u	618	C10-C9-C1	36	2.439	916.9	-298.9
9	B_{2u}	618	C5-C6-C7-C8	48	0.327	567.5	50.5
8	A_g	512	C9-C10-C5	39	2.439	916.9	-404.9
7	B_{3g}	506	C5-C6-C7	41	2.230	900.4	-394.4
6	B_{3u}	476	C9-C1-C2-C3	44	0.325	566.1	-90.1
5	B_{2g}	461	C10-C5-C6-C7	47	0.325	566.1	-105.1
4	B_{1g}	386	C10-C9-C1-C2	43	0.340	565.7	-179.7
3	B_{1u}	359	C1-C2-C3	38	2.230	900.4	-541.4
2	A_u	195	C9-C10-C5-C6	46	0.340	565.7	-370.7
1	B_{3u}	176	C8-C9-C10-C4	42	0.378	371.4	-195.4

[a] Bending and torsion force constants are given in (mdyn Å)/rad^2

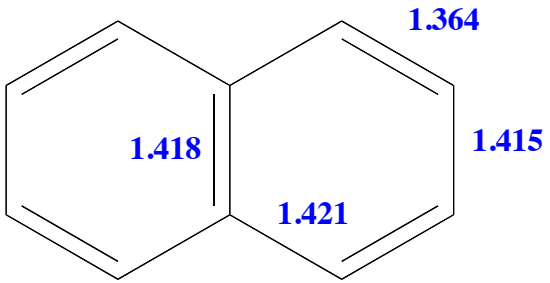


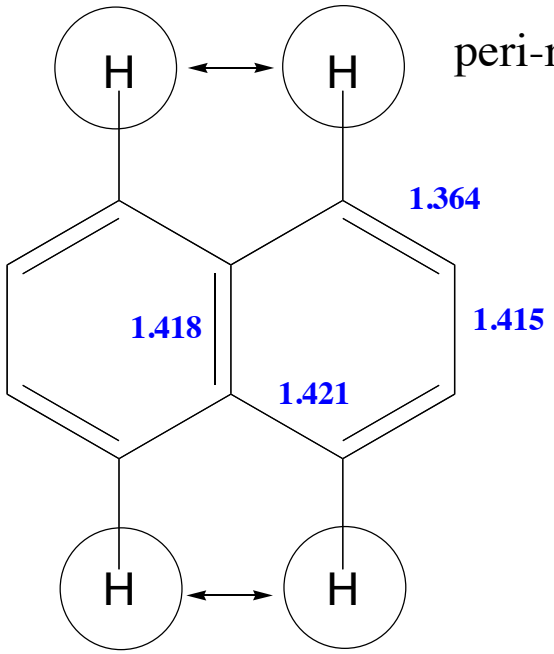
Napthalene



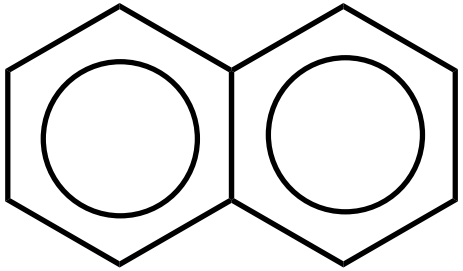
Adiabatic Connection Schemes

Napthalene: Bond lengths do not always reflect the bond strength

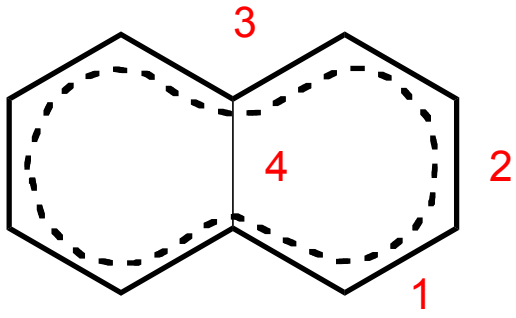




competing benzene rings

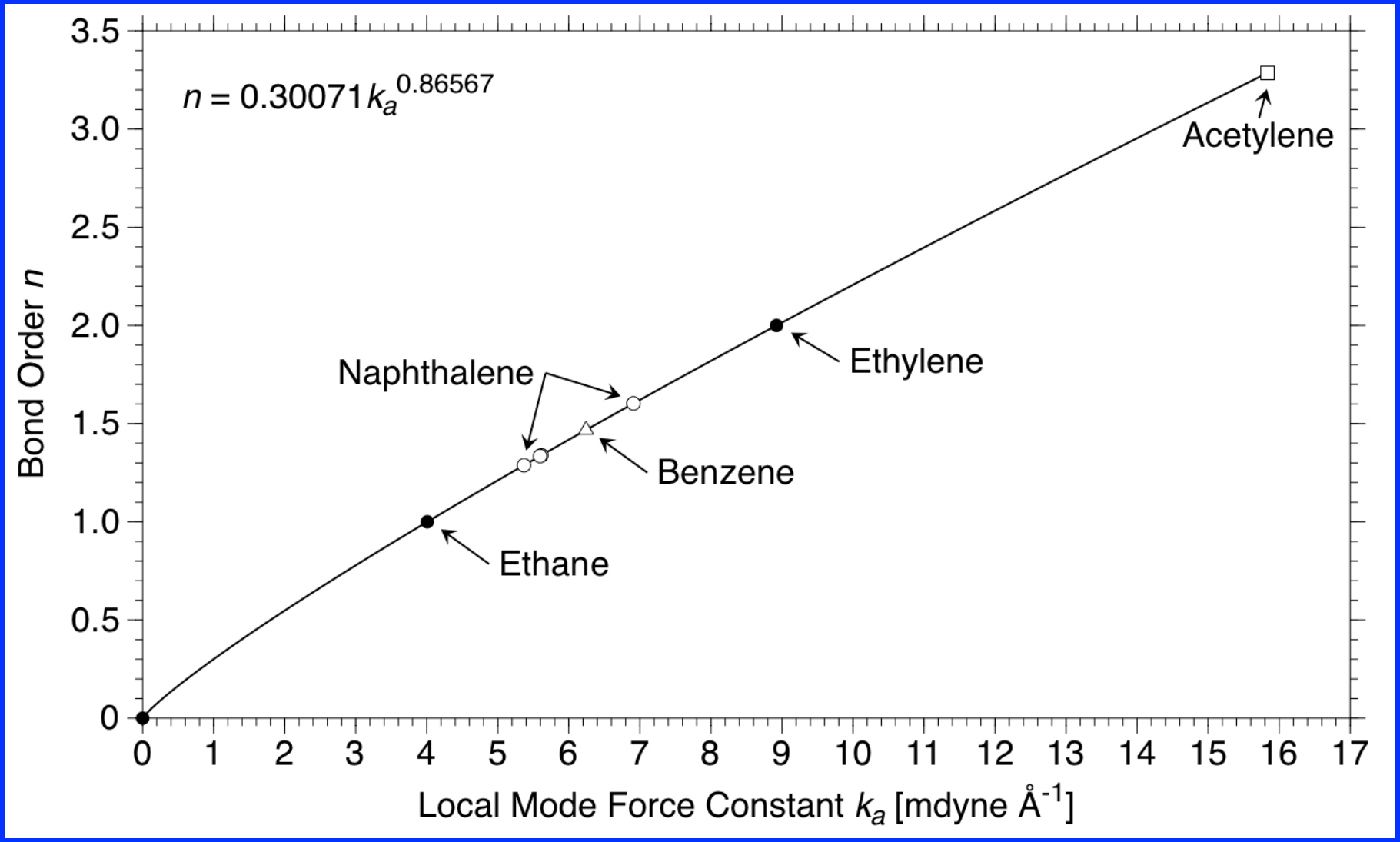


?



delocalized 10 π system

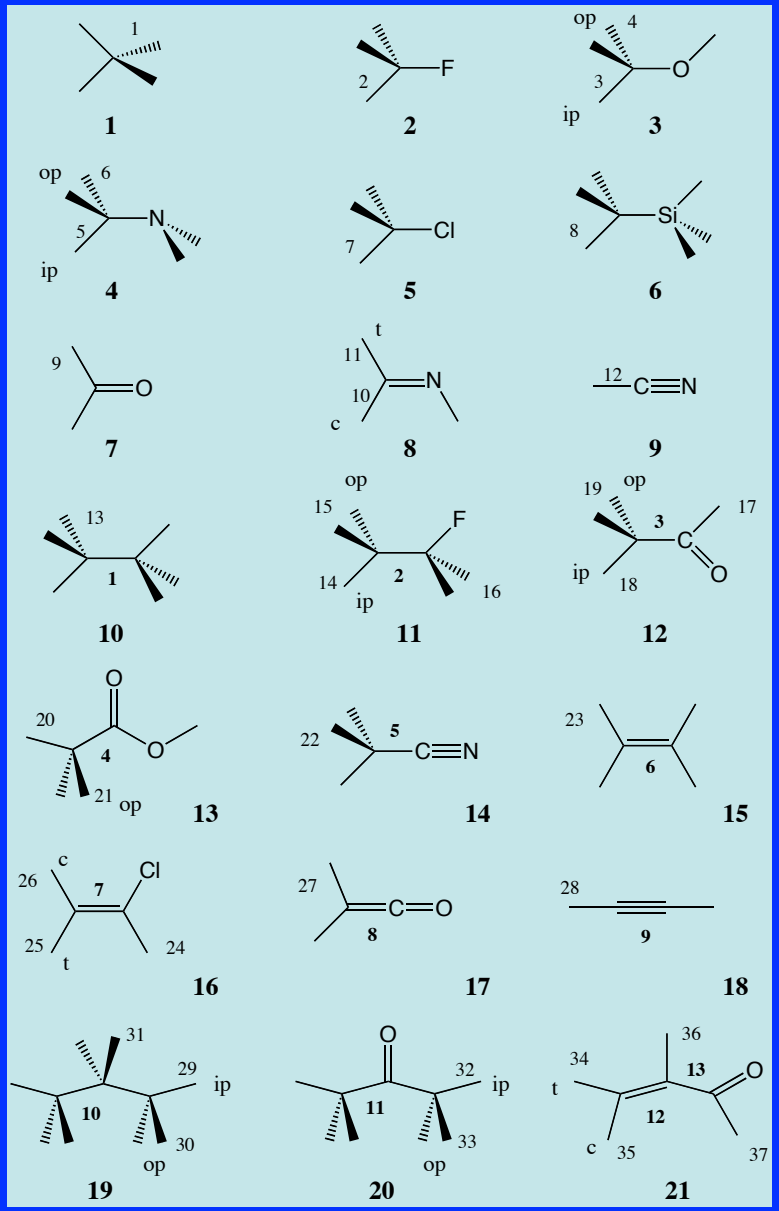
Napthalene: Determination of a bond order

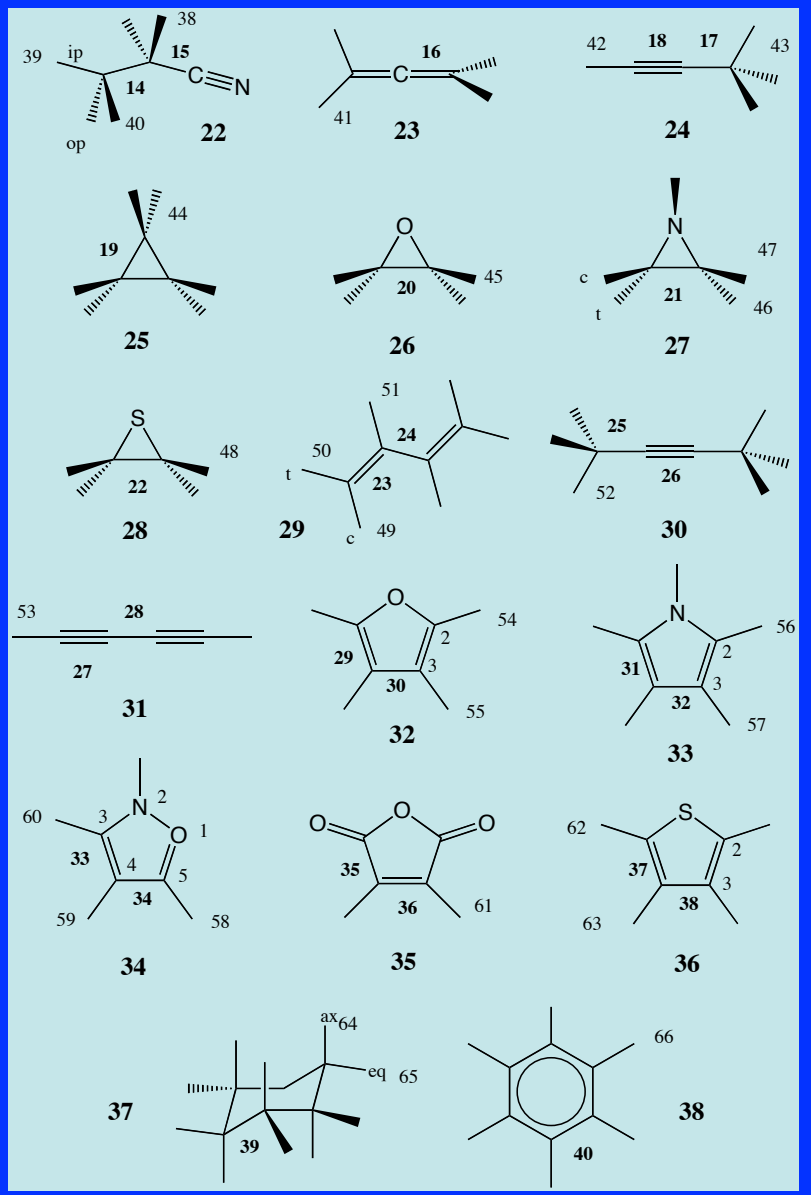


Badger Rule

for

Polyatomic Molecules


1
2
F
3
op
4
O
ip
4
op
6
N
5
ip
5
Cl
7
6
Si
8
7
9
O
8
t
11
10
N
c
9
12
C≡N
10
13
1
11
op
15
F
14
2
ip
16
12
19
op
3
17
C
O
ip
18
13
O
20
4
O
21
op
14
5
22
C≡N
15
23
6
16
c
26
7
Cl
25
t
24
17
27
C=O
8
18
28
9
19
31
29
ip
10
30
op
20
O
32
ip
11
33
op
21
36
34
13
O
t
12
c
35
37


38
39
ip
15
C≡N
14
40
op
22
16
C
41
23
42
18
17
43
24
44
19
25
O
20
45
26
N
47
c
21
t
46
27
S
48
22
28
51
24
50
t
23
c
49
29
25
52
26
30
53
28
27
31
O
2
54
29
3
30
55
32
N
56
2
31
3
32
57
33
60
N
2
3
O
1
33
4
5
34
59
58
34
O
O
O
35
36
61
35
62
S
2
37
3
38
63
36
ax
64
eq
65
39
37
66
40
38

For the description of Chemical Bonds

$4\pi^2\mu\ \nu^2 = k$

electronic effect

Stretching Force Constants

$\nu^2 = k / (4\pi^2\mu)$

are more useful than

Stretching Frequencies

electronic and mass effect

Force constant - bond length relationship

For diatomics AB, Badger's Rule, 1934

$k_e (r_e - d_{ij})^3 = \text{const}$

d_{ij} depends on the positions of atoms A and B in the periodic table

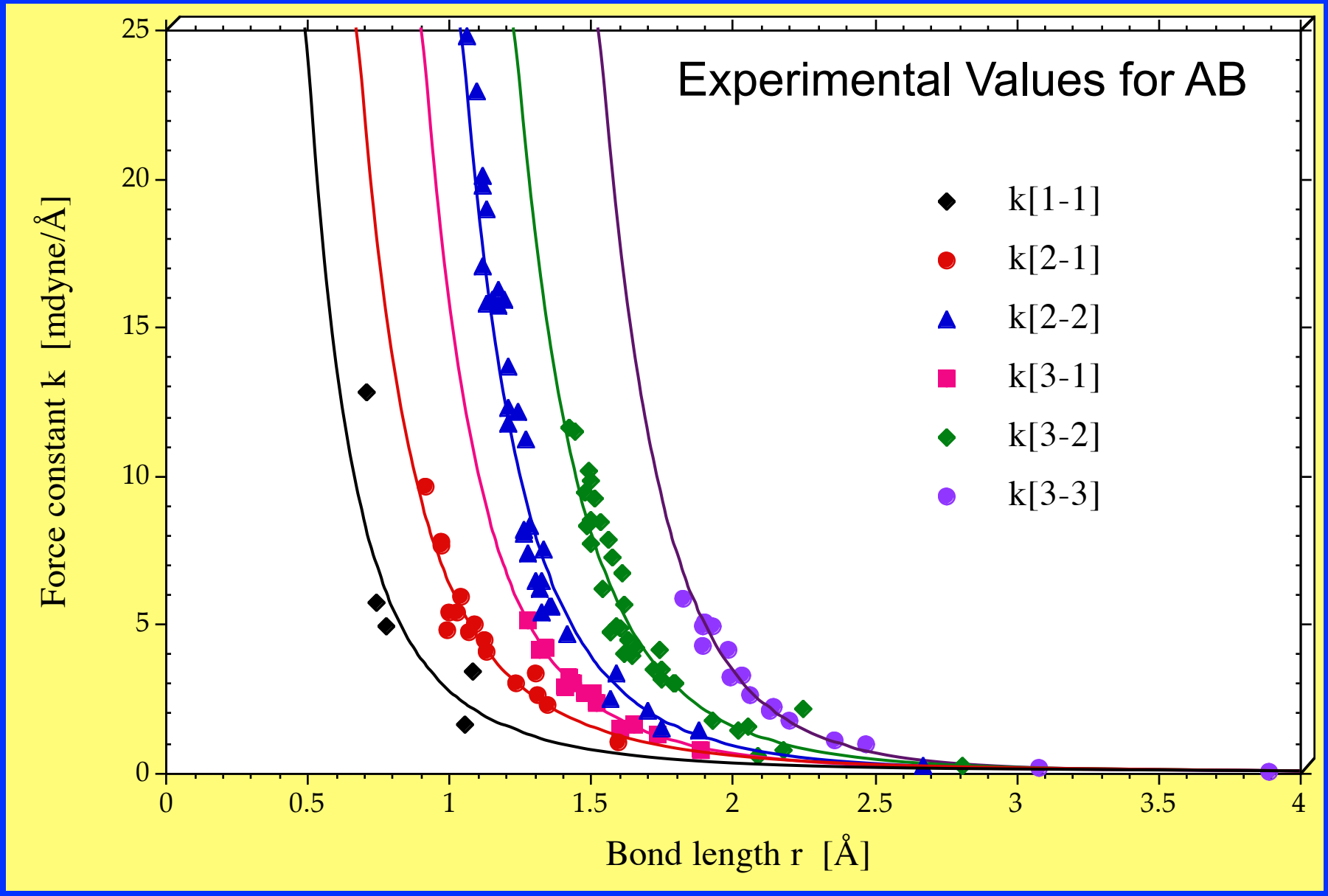
effective bond length

Generalization requires local force constants !

$k_e (r_e - d)^p = \text{const}; \; r_e = a \, k_e^{-1/p} + b$

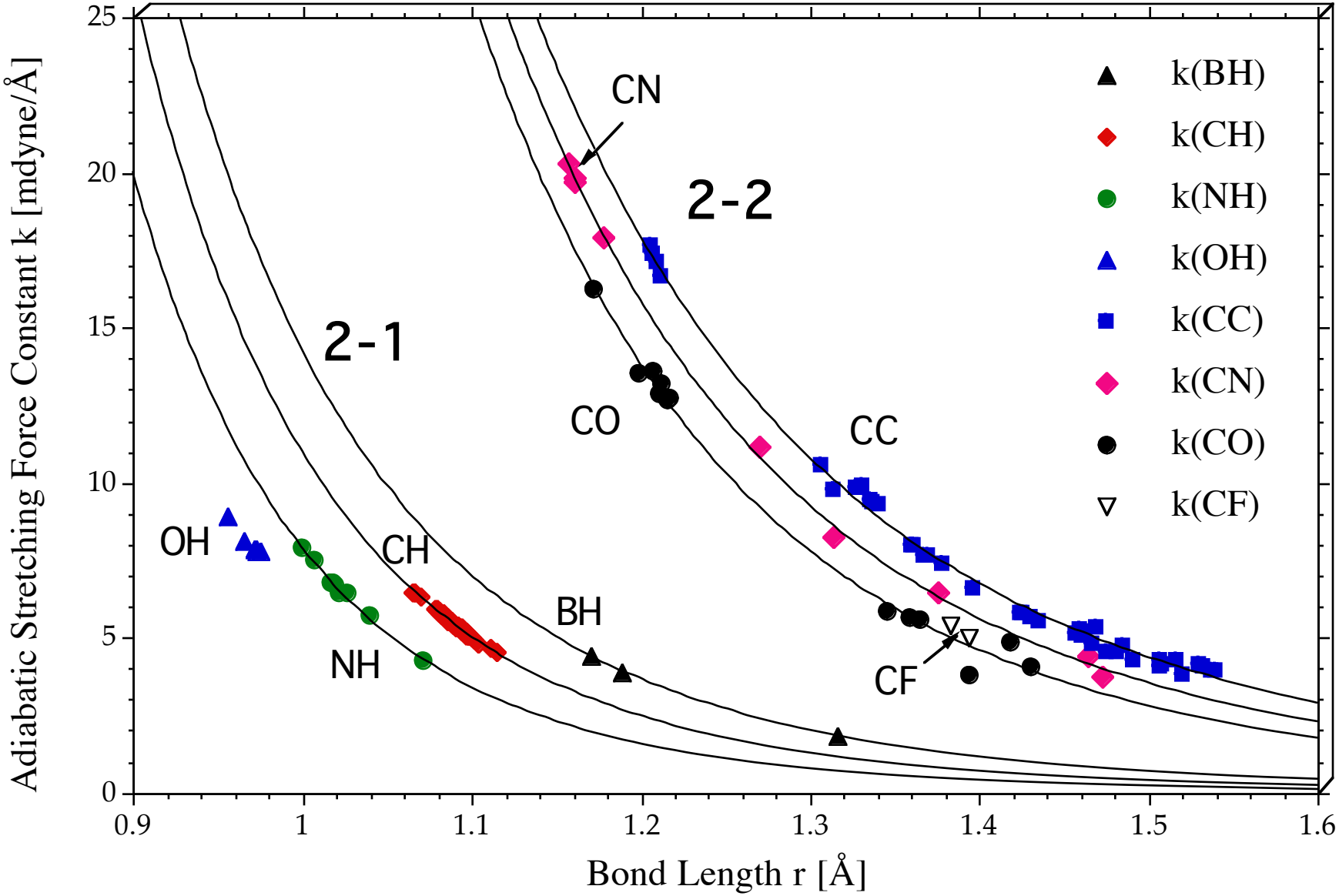
with $2 \le p \le 6$, similar equations for ω_e

Badger Relationships for 120 Diatomic Molecules

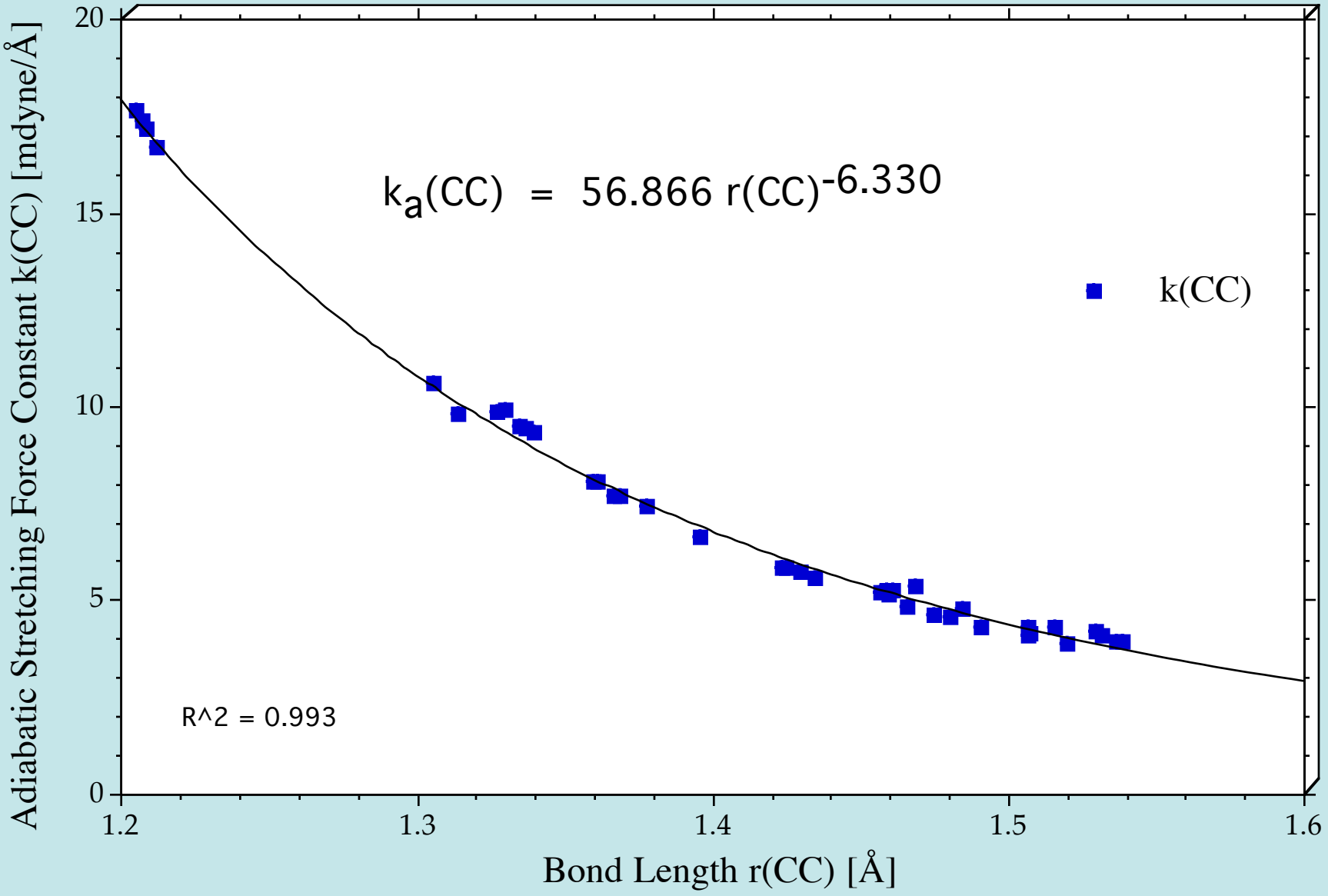


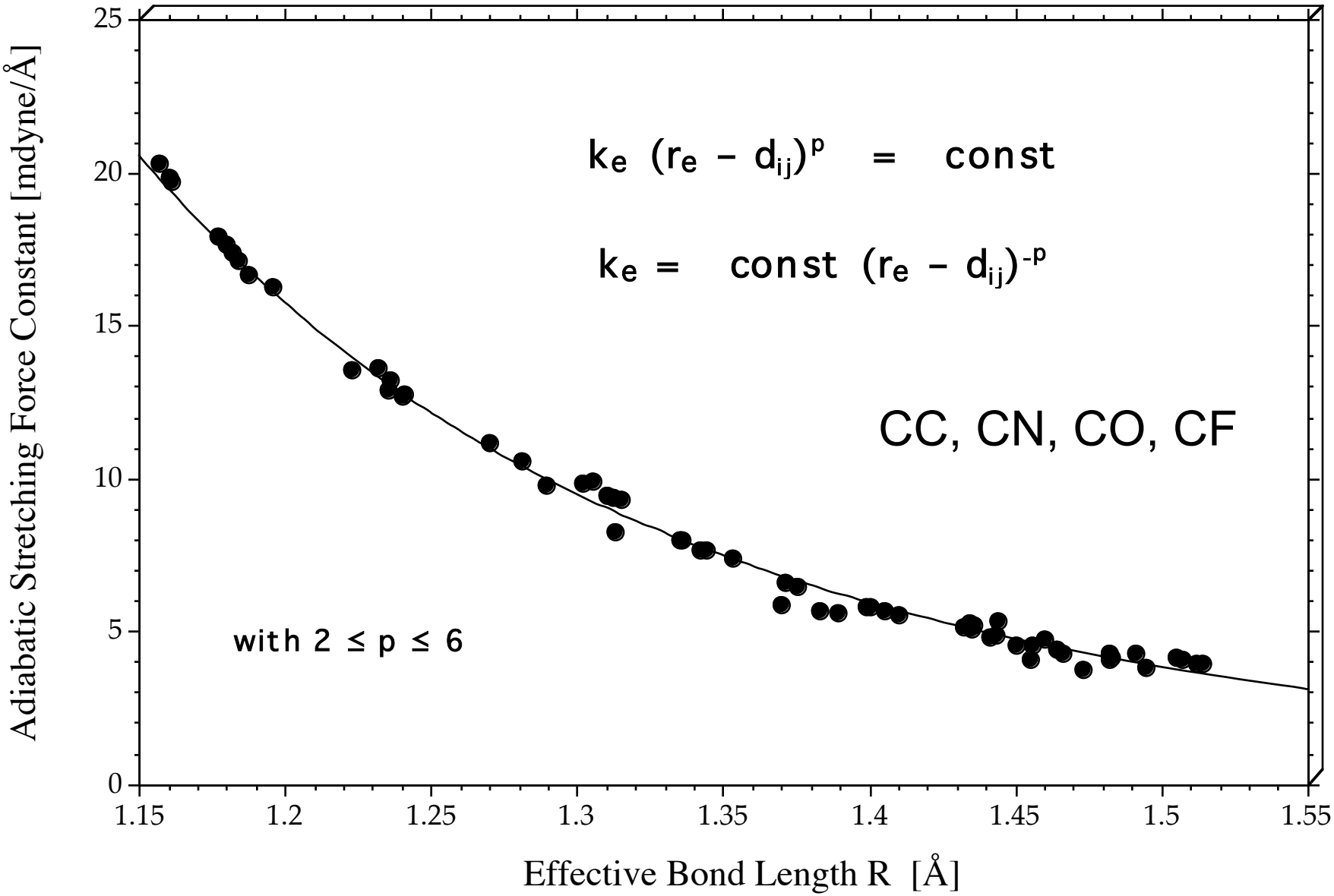
Period i - Period j atom-atom bonding

Experimental AICoMs



Extending the Badger Rule from Diatomics to Polyatomics



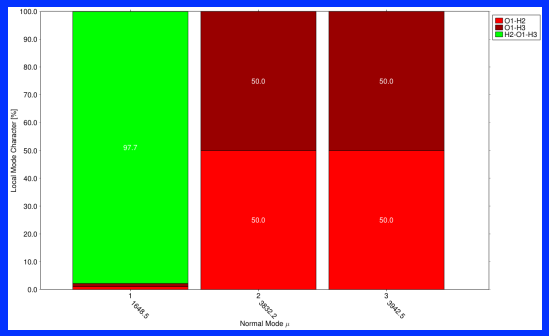

Adiabatic Stretching Force Constant [mdyne/Å]
25
20
15
10
5
0
1.15
1.2
1.25
1.3
1.35
1.4
1.45
1.5
1.55
Effective Bond Length R [Å]
$k_e\ (r_e - d_{ij})^p = \text{const}$
$k_e = \text{const}\ (r_e - d_{ij})^{-p}$
CC, CN, CO, CF
with $2 \le p \le 6$

Rules

for

Mode-Mode Coupling

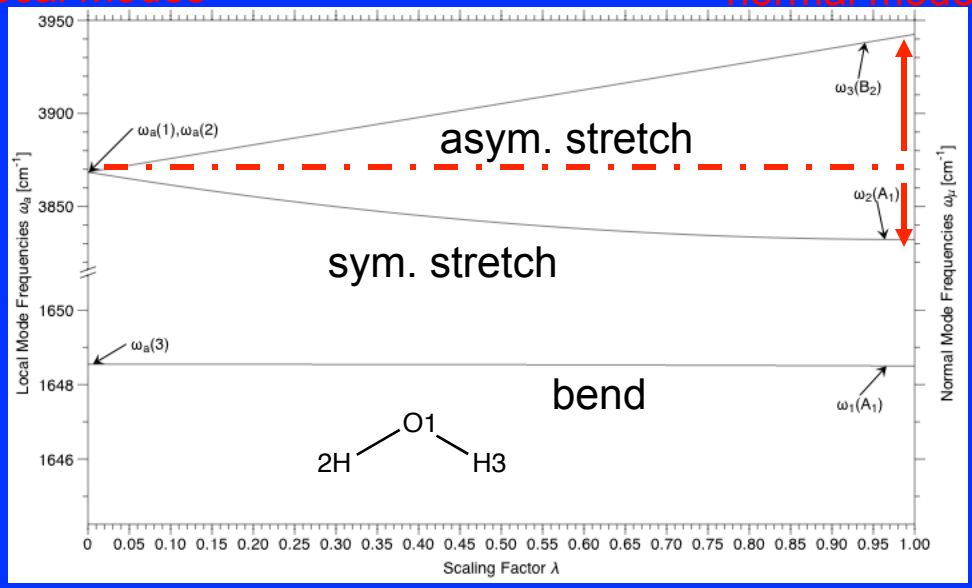
Adiabatic Connection Scheme and Coupling Frequencies



red: stretches
green: bends

local modes

normal modes

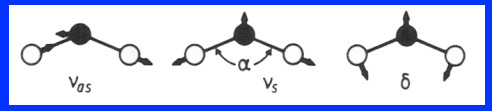


Coupling Frequencies

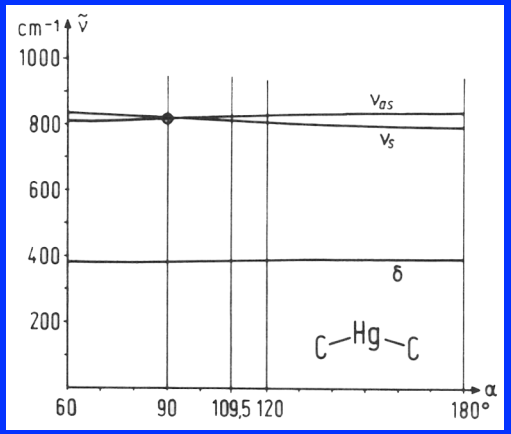
μ	k_a [mdyn Å^{-1}]	ω_a [cm^{-1}]	ω_μ [cm^{-1}]	ω_{coup} [cm^{-1}]	Param.	Param. #
3	8.359	3868.4	3942.5	74.1	O1-H2	1
2	8.359	3868.4	3832.2	-36.2	O1-H3	2
1	0.692	1648.5	1648.5	0.0	H2-O1-H3	3

Water

Coupling Rules

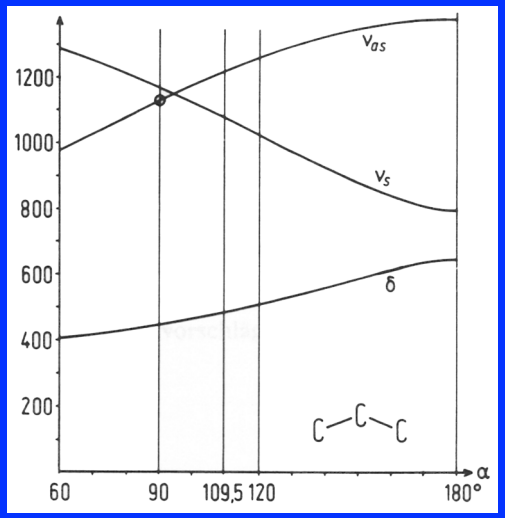


Light -heavy -light



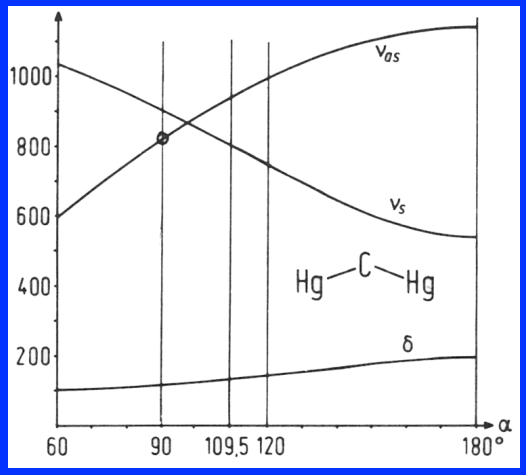
small coupling

Equal masses



largest coupling

Heavy - light - heavy



large coupling

the mode vectors have to have parallel components;
if they are orthogonal they do not couple

Local Mode

Intensities

Infrared Intensity of Normal Vibrational Modes

$$I_\mu = (8\pi^3 N_A g/3hc)\left|\frac{\partial \boldsymbol{\mu}}{\partial Q_i}\right|^2$$

$$I_\mu = C(\boldsymbol{\delta}_\mu)^\dagger \ \boldsymbol{\delta}_\mu$$

$$\boldsymbol{\delta} = \boldsymbol{\Delta} \ \boldsymbol{L}(\mathbf{M}^R)^{-1/2}$$

with

$$\mathbf{M}^R = \mathbf{L}^\dagger \mathbf{M} \mathbf{L}$$

and $\boldsymbol{\Delta}$ being the $3 \times 3N$ dipole moment derivative matrix (atomic polar tensor, APT)

Infrared Intensity of Local Vibrational Modes

$$\boldsymbol{\delta} = \boldsymbol{\Delta}\ \mathbf{C}\ \mathbf{D}(\mathbf{M}^R)^{-1/2}$$

$$\boldsymbol{\delta} = \boldsymbol{\Delta}\ \left(\mathbf{M}^{-1}\mathbf{B}^\dagger\mathbf{G}^{-1}\right)\ \mathbf{D}(\mathbf{M}^R)^{-1/2}$$

Application of the adiabatic approximation $\mathbf{D}_{\lambda=0} = \mathbf{I}$, $\mathbf{M}^R_{\lambda=0} = \mathbf{G}_d^{-1}$, $\mathbf{G}_{\lambda=0} = \mathbf{G}_d$ leads to

$$\begin{aligned}\boldsymbol{\delta}^a &= \boldsymbol{\Delta}\mathbf{M}^{-1}\mathbf{B}^\dagger\mathbf{G}_d^{-1}\mathbf{G}_d^{1/2} \\ &= \boldsymbol{\Delta}\mathbf{M}^{-1}\mathbf{B}^\dagger\mathbf{G}_d^{-1/2}\end{aligned}$$

i) isotope-independent
ii) parameter-independent.

Because of the parameter-independence, $\boldsymbol{\delta}$ can be defined for each local mode n

$$\boldsymbol{\delta}^a_n = \boldsymbol{\Delta}\mathbf{M}^{-1}\mathbf{b}^\dagger_n/\sqrt{G_{nn}}$$

Intensity of local mode n:

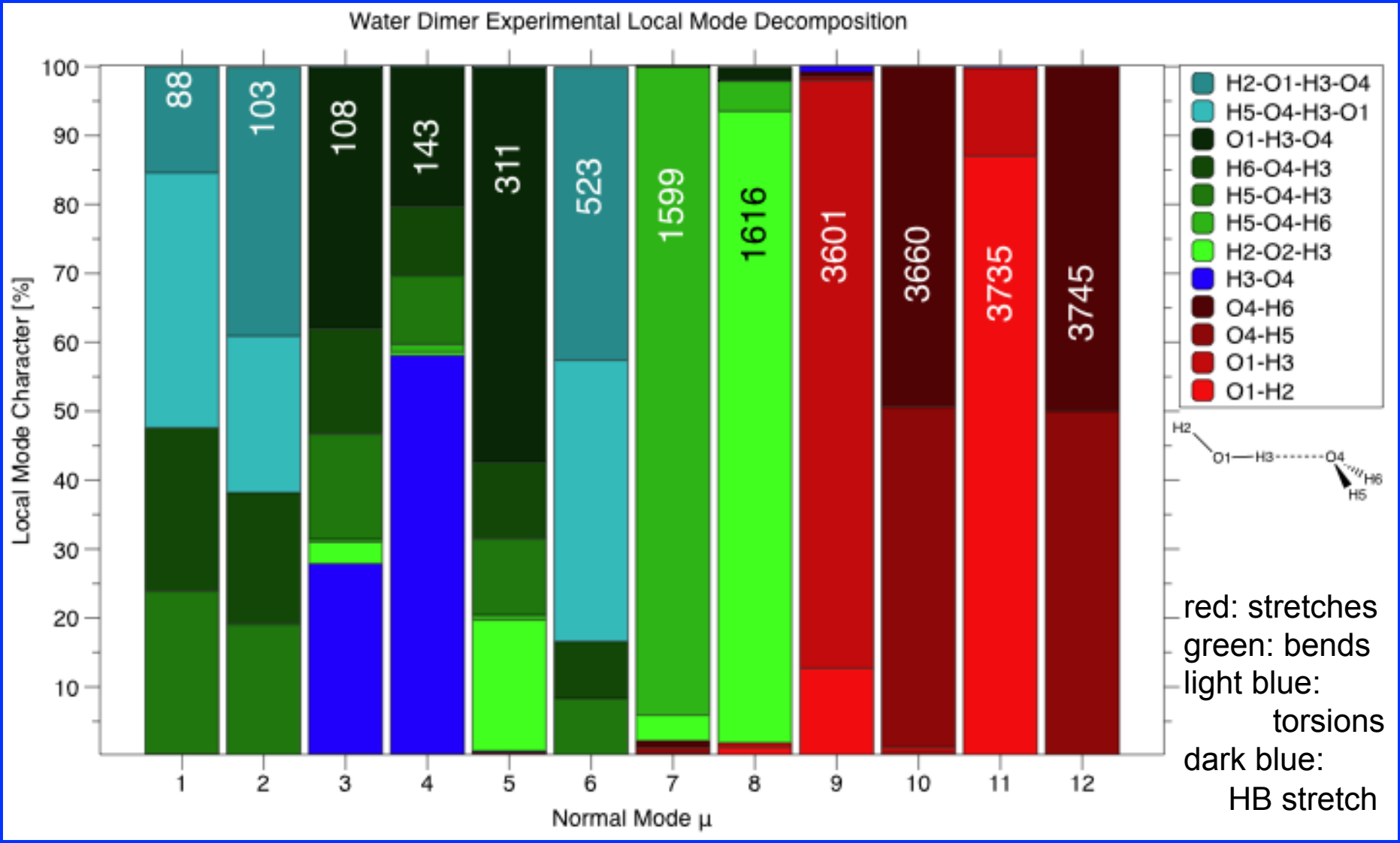
$$I^a_n = C(\boldsymbol{\delta}^a_n)^\dagger\boldsymbol{\delta}^a_n$$

Infrared Intensity of Local Vibrational Modes

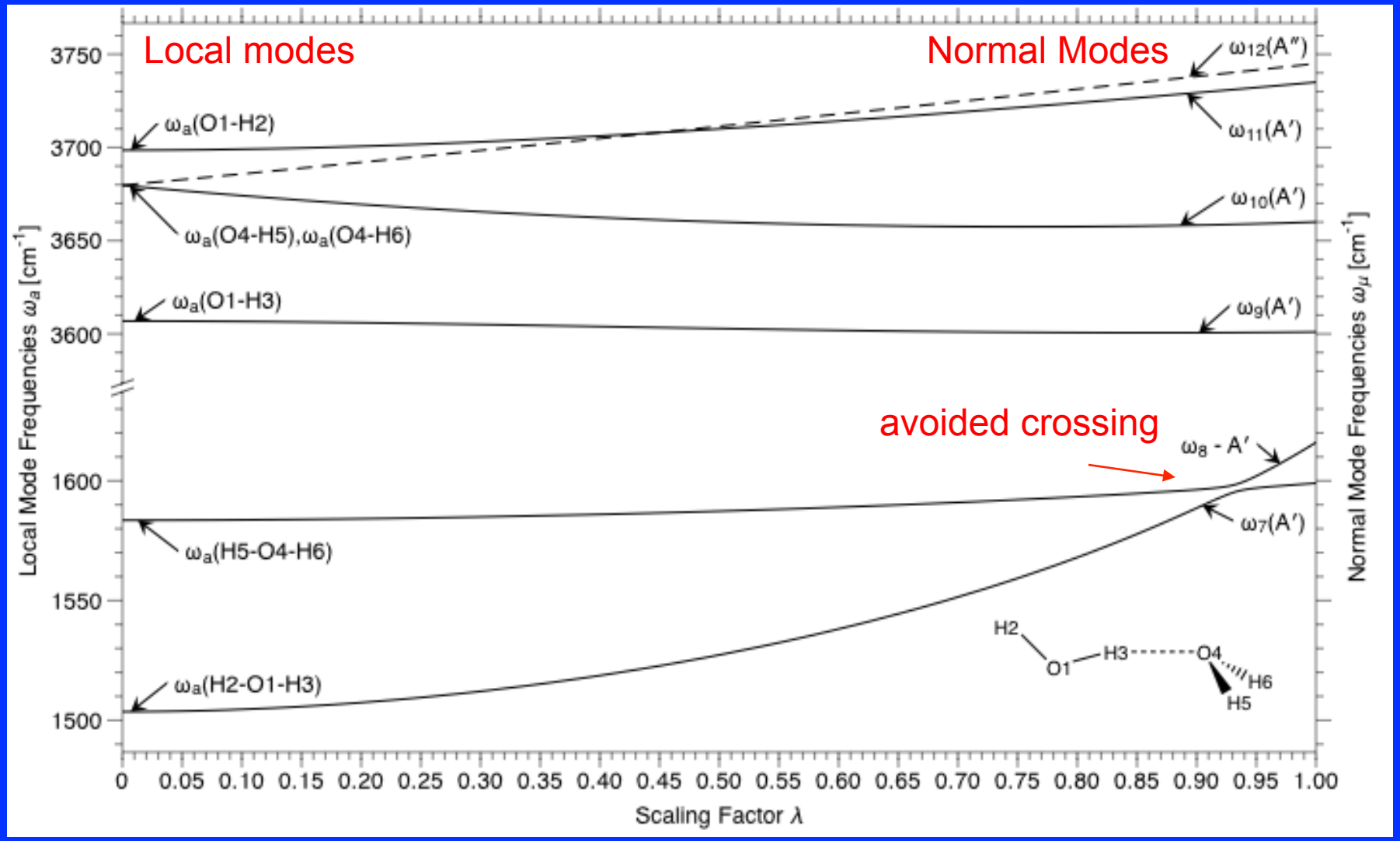
Molecule	Parameter	I_n[a] [km/mol]	μ	I_μ [km/mol]	Molecule	Parameter	I_n[a] [km/mol]	μ	I_μ [km/mol]
Internal Coordinate set 1									
H-O-H	H-O	23.4868	3	40.8595	H-O-D	H-O	23.4868	3	24.7171
	H-O	23.4868	2	3.2361		D-O	14.9527	2	11.2932
	H-O-H	69.1712	1	69.5078		H-O-D	59.8634	1	59.5745
Internal Coordinate set 2									
H-O-H	H-O	23.4868	3	40.8595	H-O-D	H-O	23.4868	3	24.7171
	H-O	23.4868	2	3.2361		D-O	14.9527	2	11.2932
	H...H		1	69.5078		H...D		1	59.5745

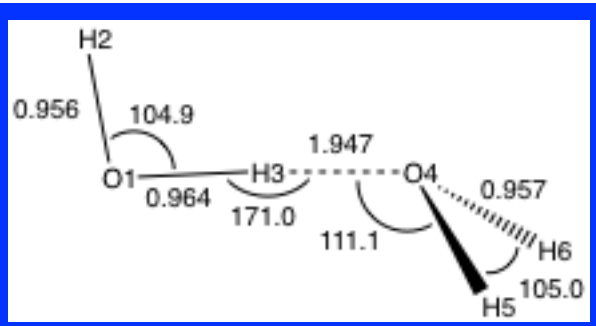
Investigation of the Hydrogen bond

Normal vibrational modes of the water dimer: Exp. frequencies

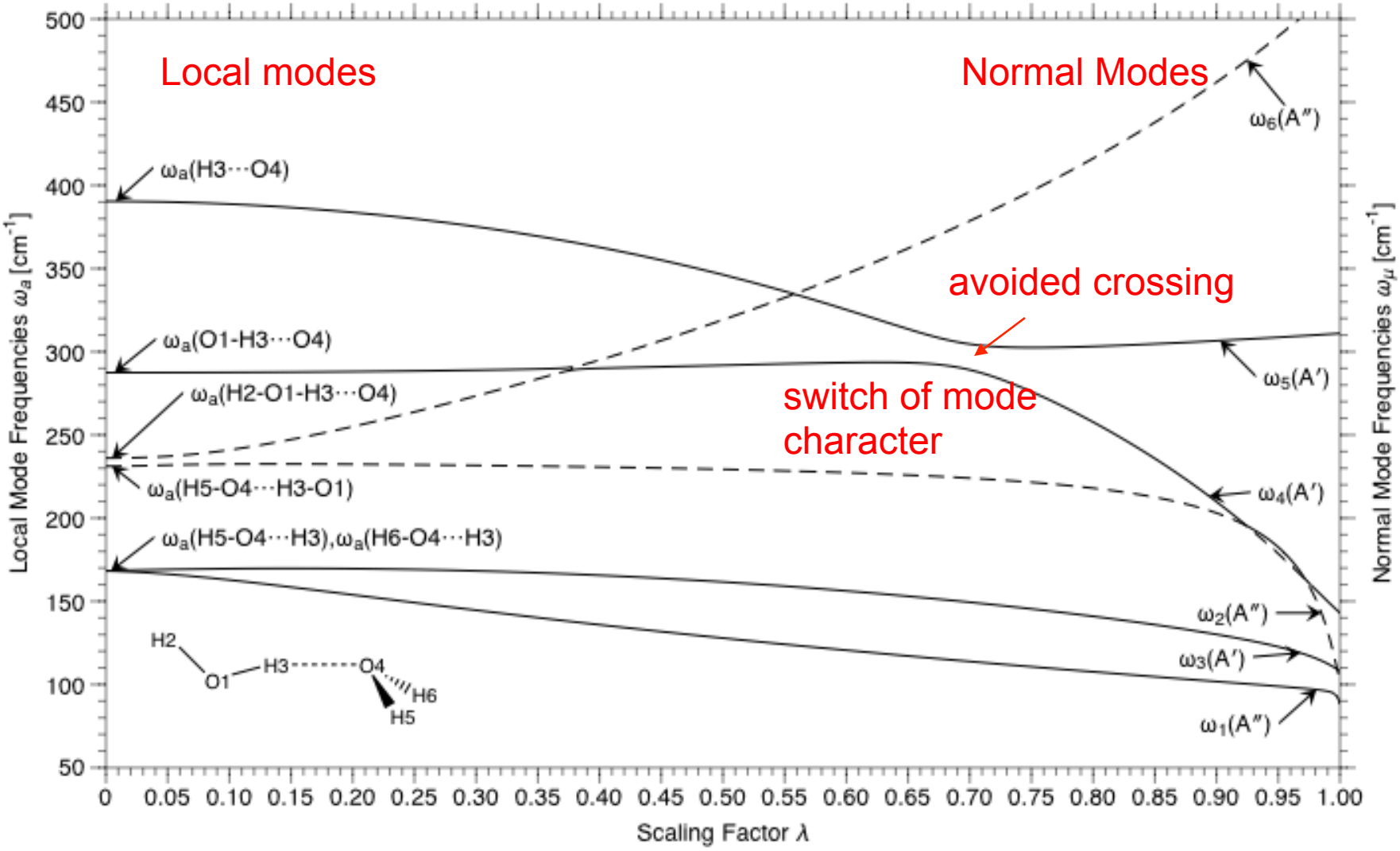


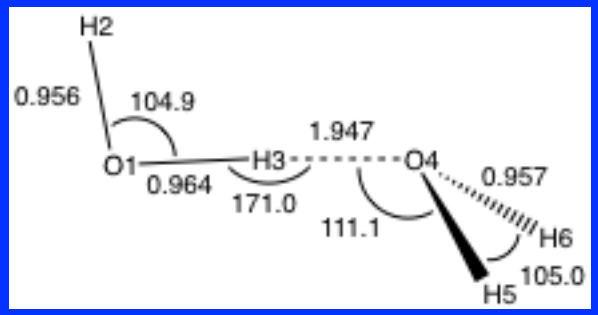
Normal mode vibrations are decomposed into local modes





Adiabatic connection scheme of the water dimer: Exp. frequencies

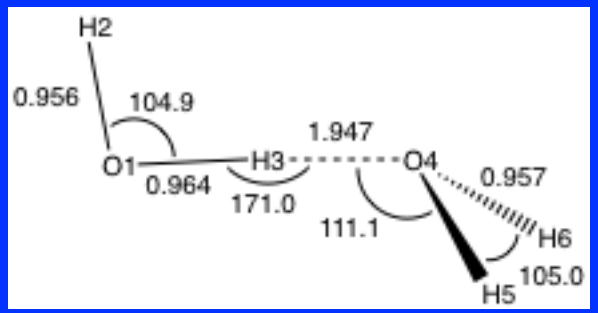


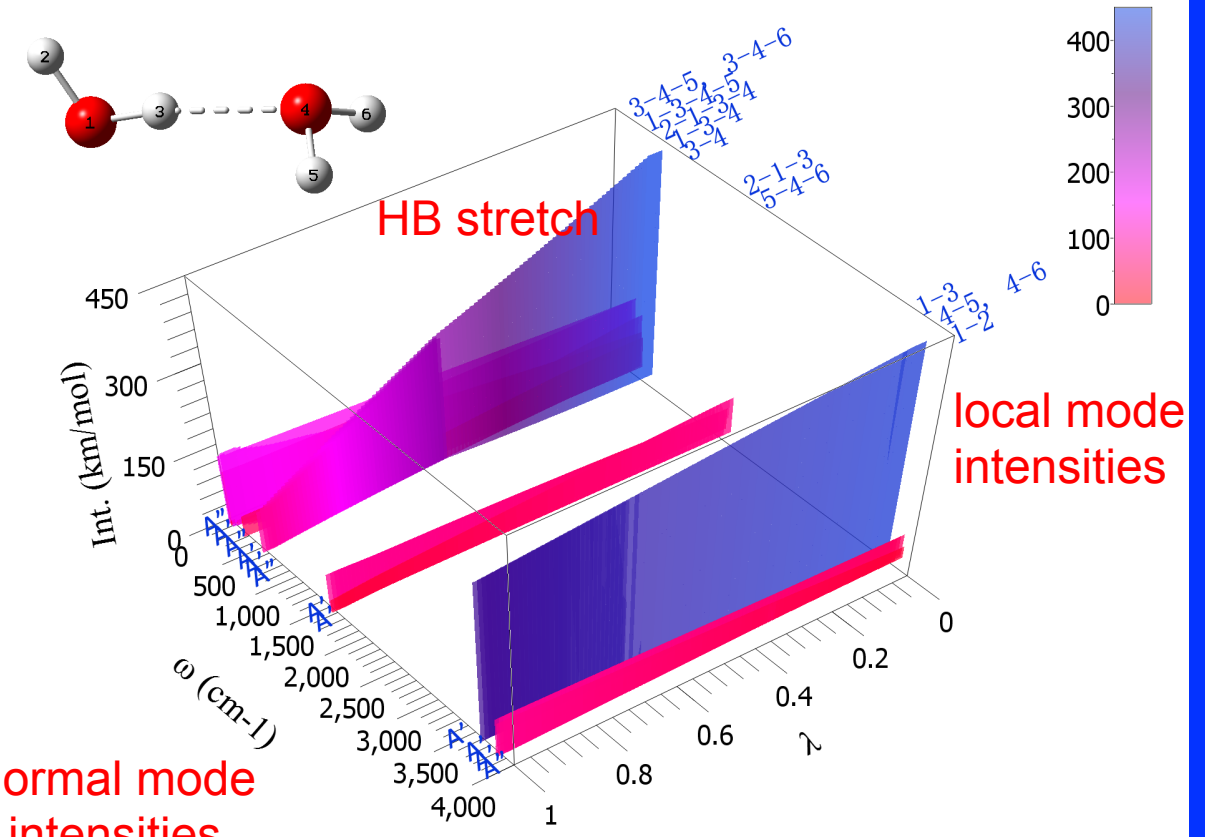


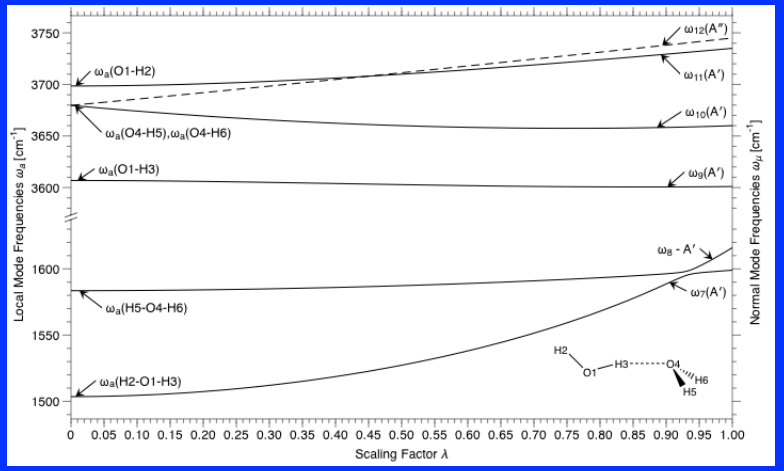
Adiabatic connection scheme of the water dimer: Exp. frequencies

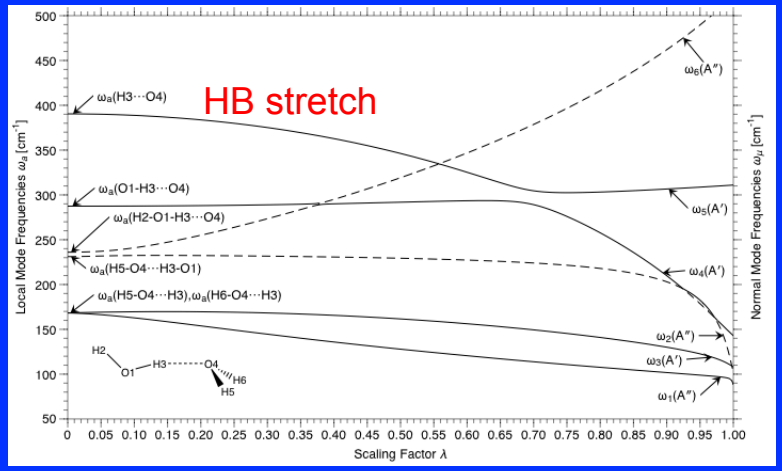
lower range

Adiabatic connection scheme including IR intensities

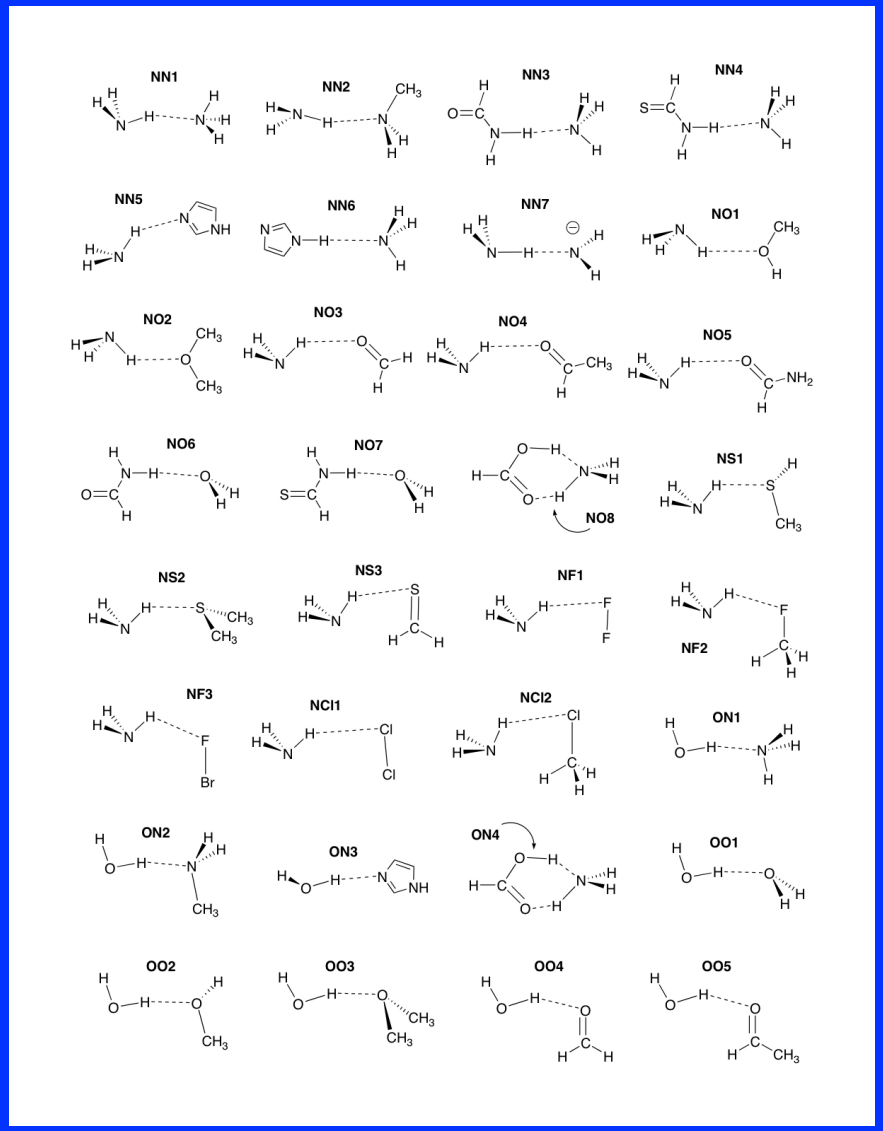


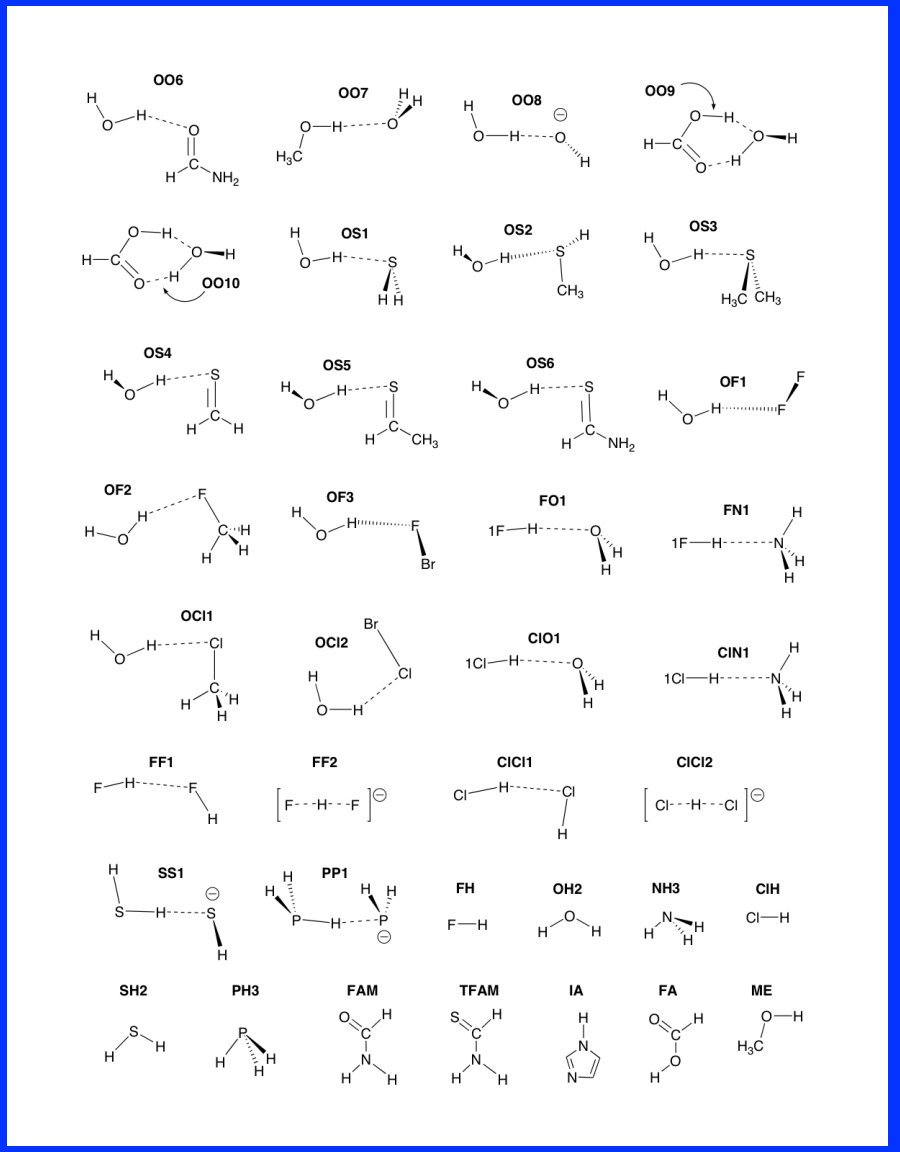




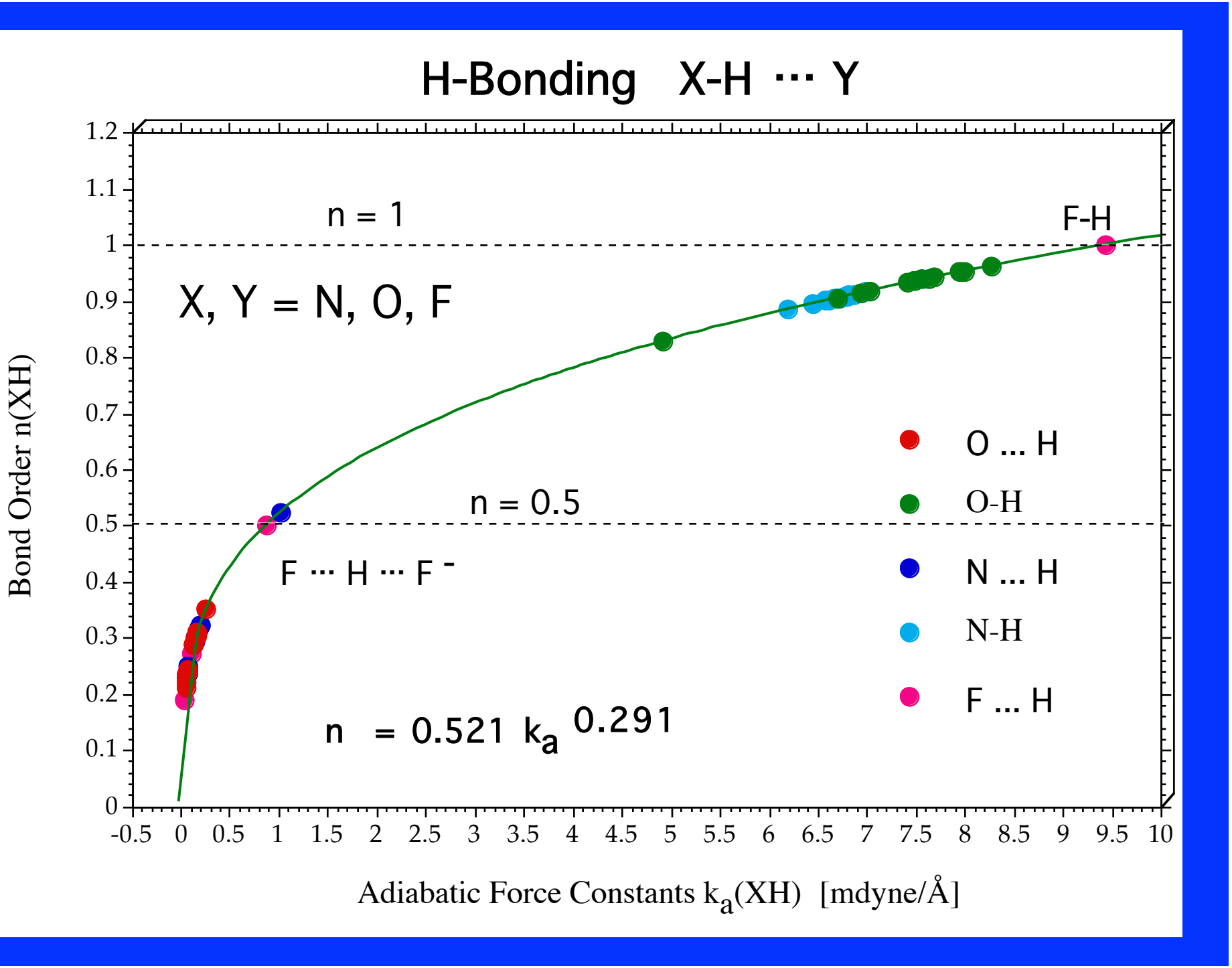


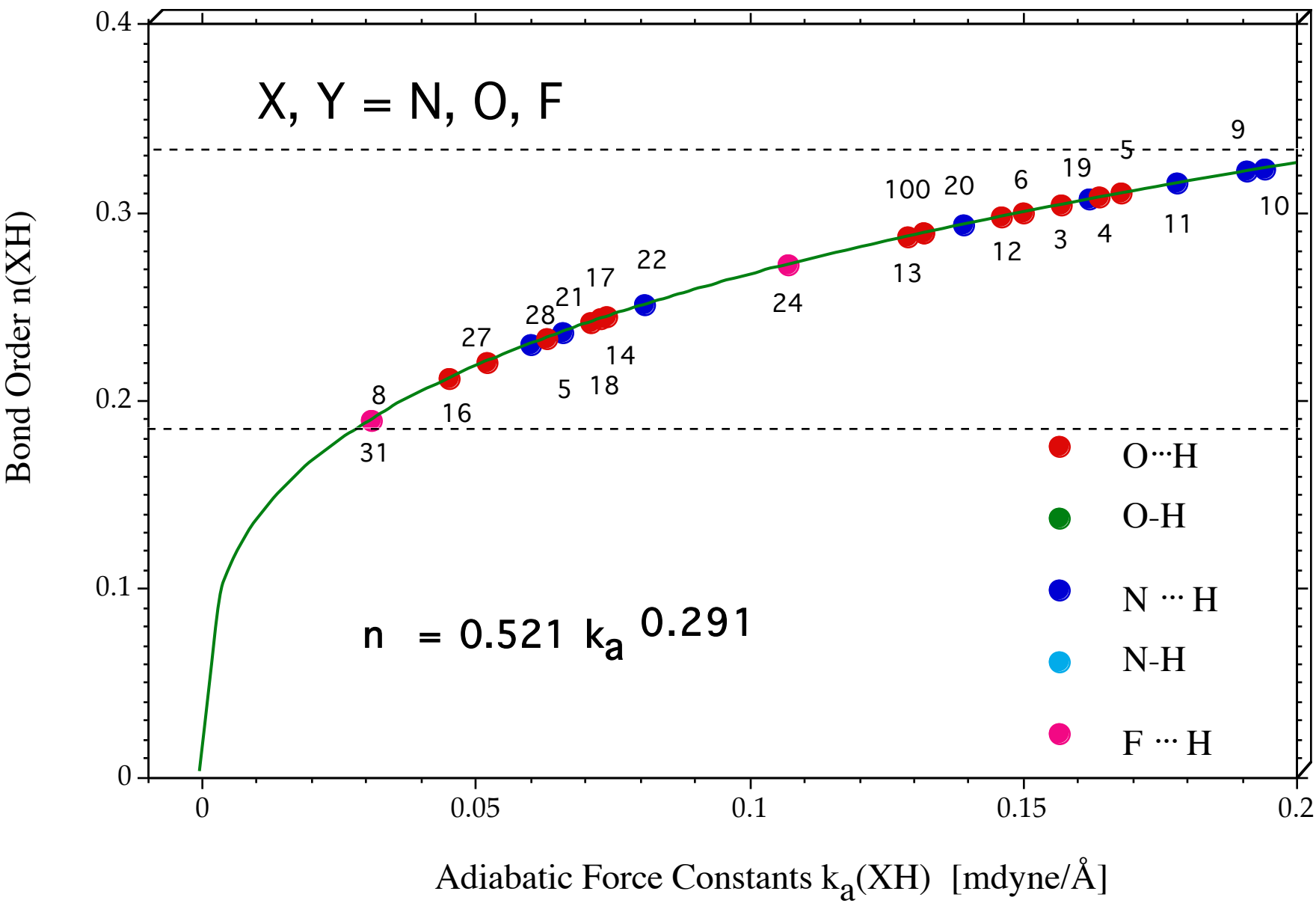
Investigation of H-bonded complexes



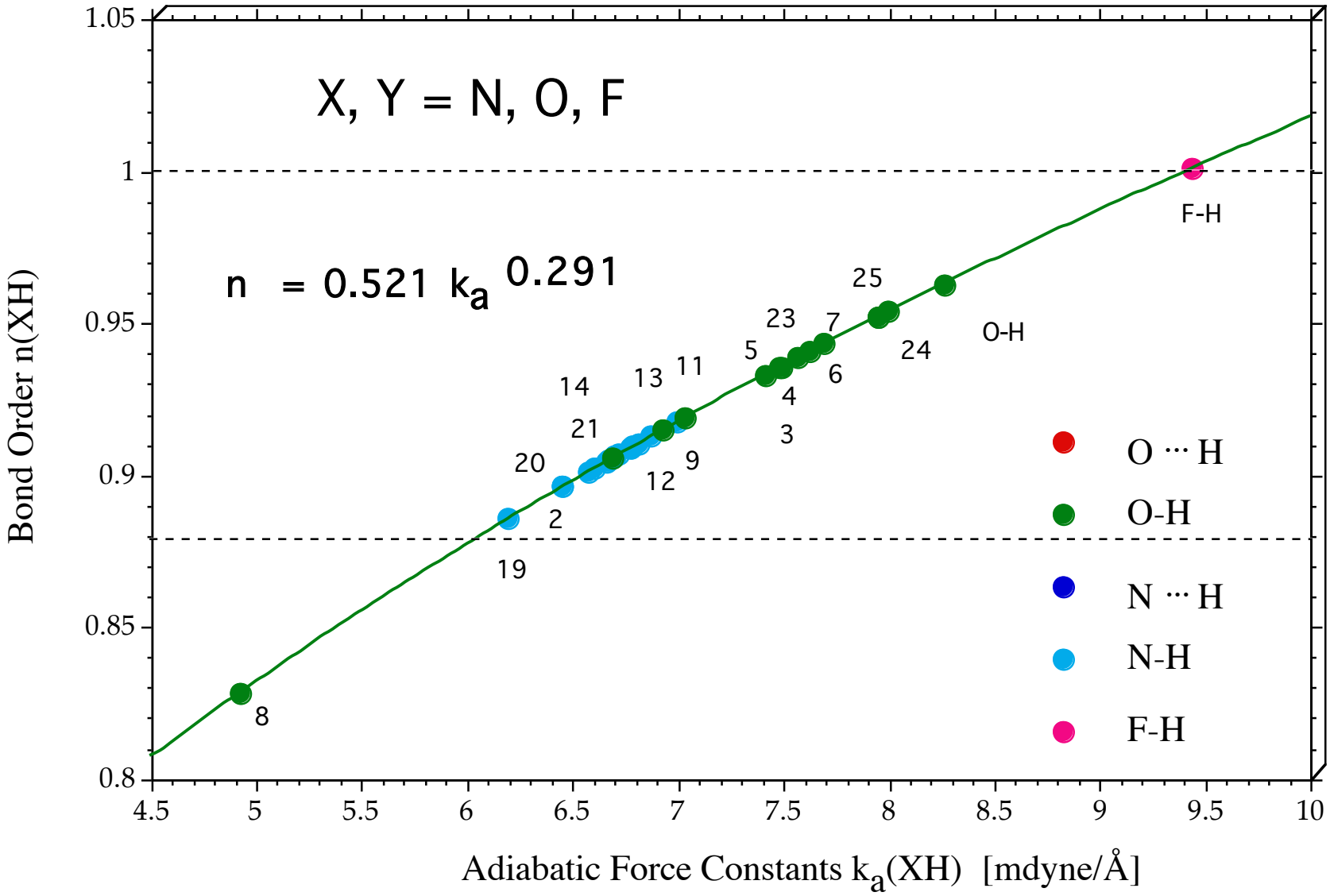


M. Freindorf, E. Kraka, and D. Cremer, Int. J. Quant. Chem. 112, 3174-3187


H-Bonding X-H ··· Y
n = 1
F-H
X, Y = N, O, F
n = 0.5
F ··· H ··· F -
n = 0.521 k_a 0.291
O ... H
O-H
N ... H
N-H
F ... H
Bond Order n(XH)
Adiabatic Force Constants k_a(XH) [mdyne/Å]
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
6.5
7
7.5
8
8.5
9
9.5
10


H-Bonding X-H ··· Y
X, Y = N, O, F
n = 0.521 k_a 0.291
Bond Order n(XH)
Adiabatic Force Constants k_a(XH) [mdyne/Å]
0.4
0.3
0.2
0.1
0
0.05
0.15
O···H
O-H
N ··· H
N-H
F ··· H
31
8
16
27
5
28
21
18
17
14
22
24
13
100
20
12
6
3
19
4
5
11
9
10

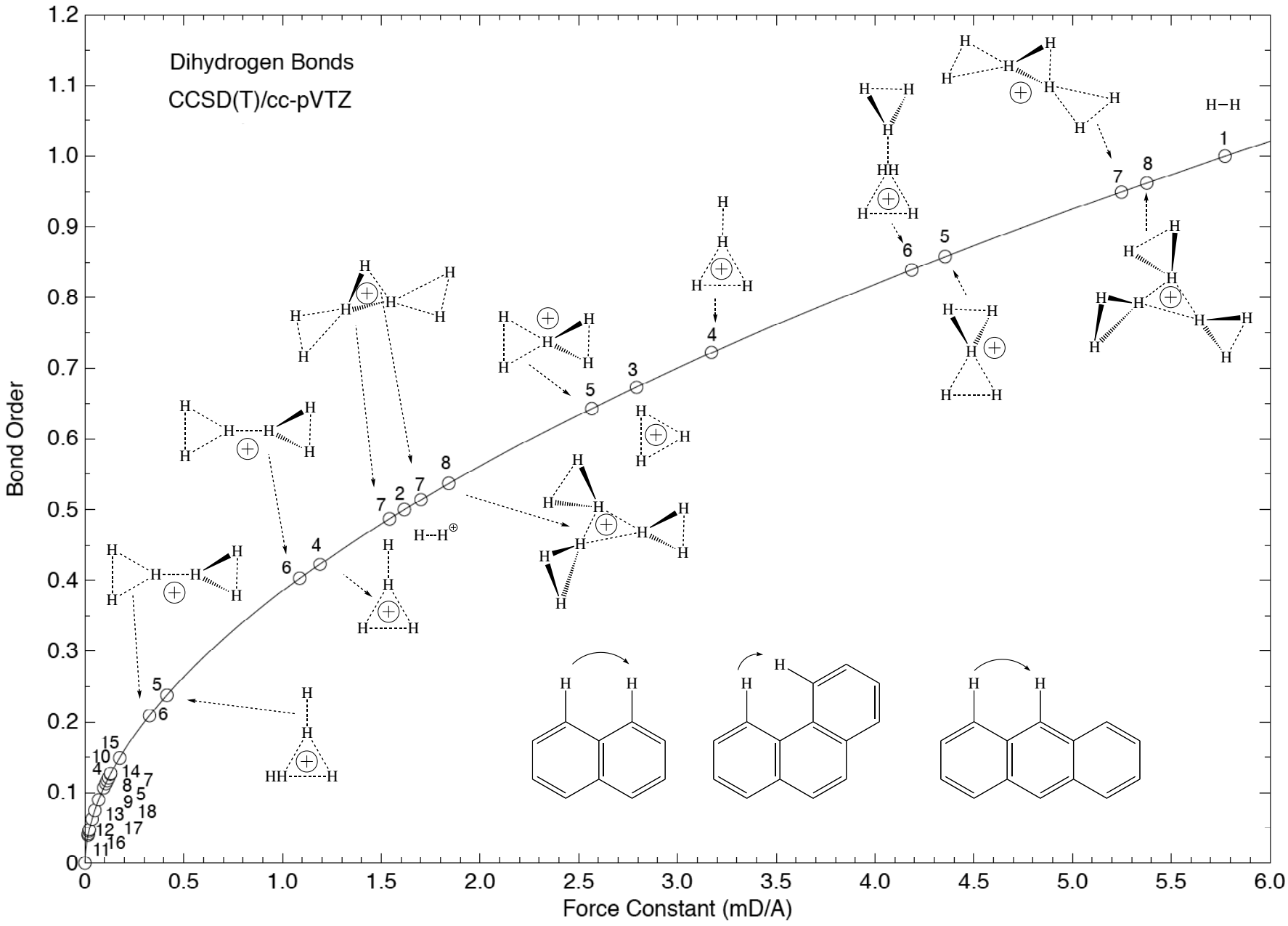
H-Bonding X-H ··· Y



M. Freindorf, E. Kraka, and D. Cremer, Int. J. Quant. Chem. 112, 3174-3187

Applications: Investigation of

- H-bonding
- Dihydrogen bonding (borazene, etc.)
- Halogen Bonding
- Agostic / anagostic Bonding
- Extremely weak / strong Bonding
- Pnicogen Bonding
- Multiple bonds in TM complexes
- Gallium multiple bonds
- Bond pseudorotation
- Adiabatic puckering for aromaticity


Dihydrogen Bonds
CCSD(T)/cc-pVTZ
Bond Order
Force Constant (mD/A)
H–H
H–H⊕

Development and Application of AICoM Local Modes

http://smu.edu/catco/

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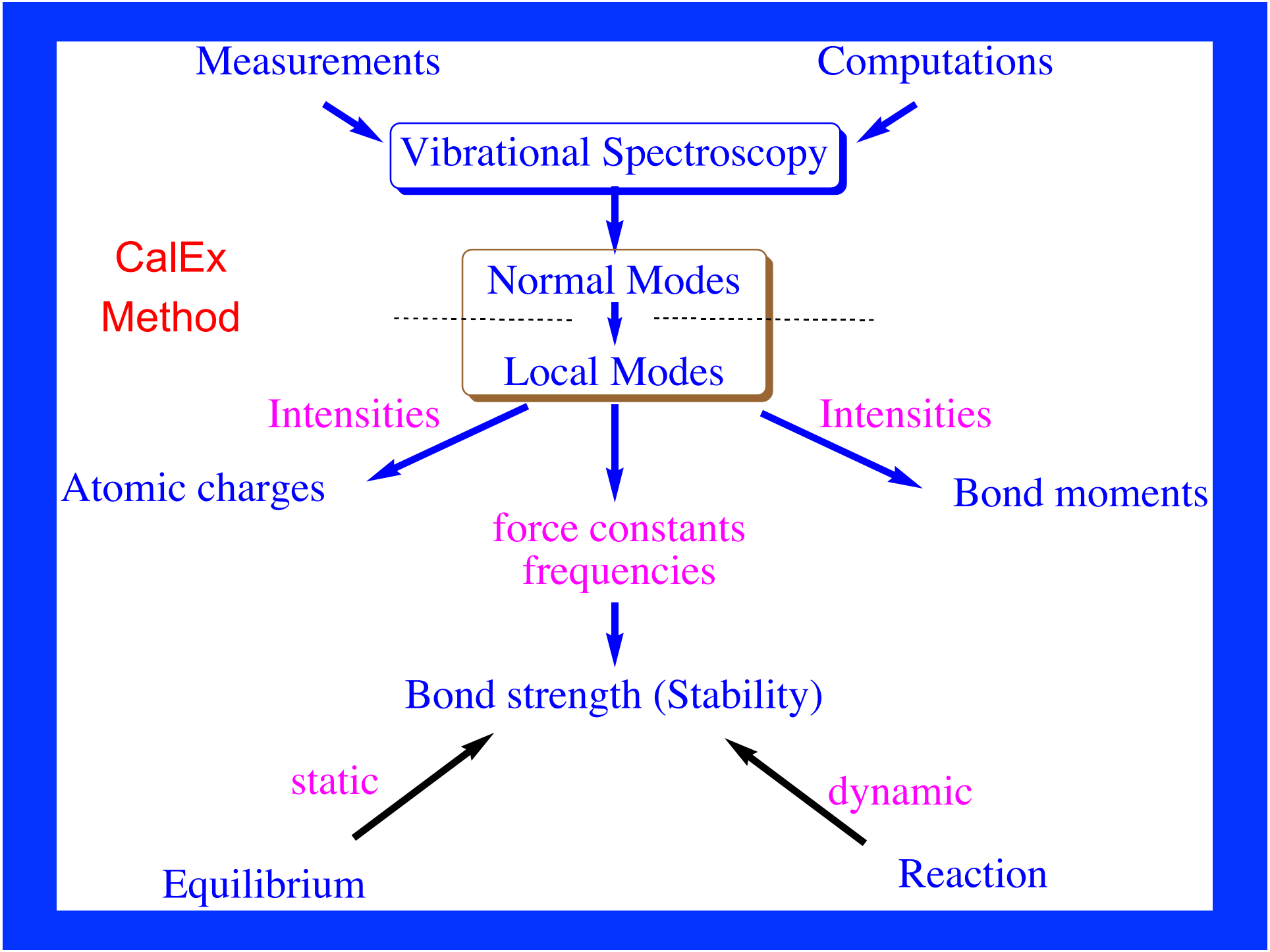
Measurements
Computations
Vibrational Spectroscopy
CalEx
Method
Normal Modes
Local Modes
Intensities
Intensities
Atomic charges
Bond moments
force constants
frequencies
Bond strength (Stability)
static
dynamic
Equilibrium
Reaction

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