NORMAL MODE ANALYSIS OF THE VIBRATIONS OF MOLECULES & CLUSTERS

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I. Thoery of "small amplitude" vibrations

  Classical

  Quantum

II. Examples

  HCO

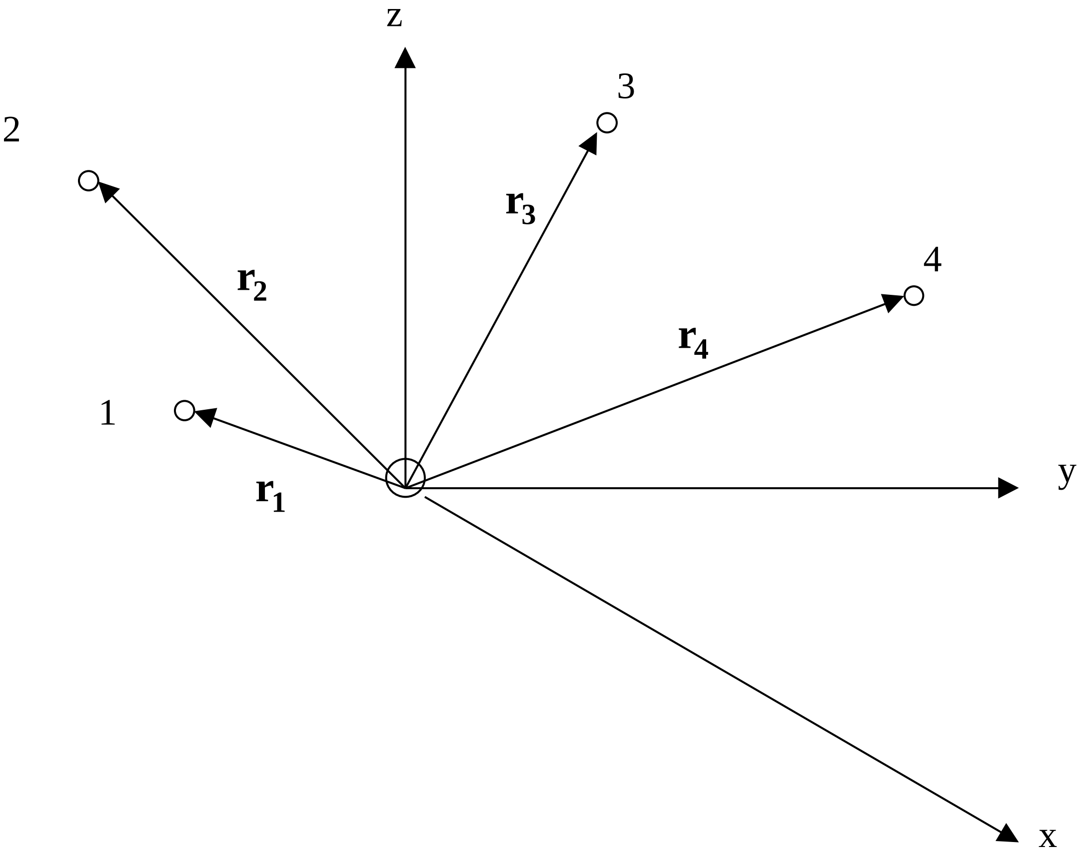
  Si(100)-(2x1)

III. What about anharmonicity and coupling?

  Thoery

  Some examples

I. Theory of Small Amplitude Vibrations



Let $\mathbf{r}_i$ be the position vector of atom *i* relative to a space-fixed coordinate system.

In general

$$T \text{ (kinetic energy) } = \sum_i \frac{P_{x_i}^2 + P_{y_i}^2 + P_{z_i}^2}{2M_i} \tag{1}$$

where M_i is the mass of atom *i*.

$$V \text{ (potential energy) } = V(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \ldots) \qquad (2)$$

but typically V depends only on the distances <u>between</u> the atoms. Thus, for a fixed geometry of the atoms, V does not depend on a rigid rotation or translation of one entire collection of atoms. (This means there are no external fields.)

Expand V about minimum (only one?) in a Taylor series:

$$\boxed{\equiv 0}$$

$$V = V\left\{u^0_{\alpha i}\right\} + \frac{1}{2}\sum_{\alpha=x,y,x}\sum_{ij}\frac{\partial^2 V}{\partial u_{\alpha,i}{}^{\partial}u_{p,j}}(u_{\alpha,i} - u^0_{\alpha,i})$$

$u_{\alpha,n}$; $\alpha = x, y, \text{or } z$ e.g., $u_{x,1} = x_1$, $\quad u_{z,29} = z_{29}$

and the coordinates of the minimum are

$$(x^0_1, y^0_1, z^0_1 \cdots x^0_N y^0_N, z^0_N) \text{ for N atoms}$$

Define <u>mass-scaled</u> cartesian coordinates

$\tilde{x}_i \equiv \sqrt{M_i}\,x_i$, etc., where M_i is the mass of atom i.

Thus,

$$T = \frac{1}{2}\sum_{i=1}^{N}(m_i\dot{x}_i^2 + m_i\dot{y}_i^2 + m_i\dot{z}_i^2)$$

$$= \frac{1}{2}\sum_{i=1}^{N}(\dot{\tilde{x}}_i^2 + \dot{\tilde{y}}_i^2 + \dot{\tilde{z}}_i^2)$$

and

$$P_{\tilde{x}_i} = \frac{\partial T}{\partial \tilde{x}_i} = \dot{\tilde{x}}_i \text{ , etc.}$$

Define <u>mass-scaled</u> cartesian displacements q_i that are indexed from 1 to 3N as follows

$$q_1 \equiv \tilde{x}_1 - \tilde{x}_1^0, q_2 = \tilde{y}_1 - \tilde{y}_1^0, \ldots, q_{3N} = \tilde{z}_N - \tilde{z}_N^0$$

Thus, (to second order)

$$V = \overset{\boxed{\equiv 0}}{V(0,0,0,\ldots 0)} + \frac{1}{2}\sum_{i=1}^{3N}\sum_{i=j}^{3N} q_i \left.\frac{\partial^2 V}{\partial q_i \partial q_j}\right|_{0,0,\ldots} q_j$$

(Why are the first derivative terms “missing”?) and

$$T = \frac{1}{2}\sum_{i=1}^{3N} \dot{q}_i^2$$

The sum T + V is the <u>Hamiltonian</u>.

$$H = \frac{1}{2}\sum_{i=1}^{3N} \dot{q}_i^2 + \frac{1}{2}\sum_{i=1}^{3N}\sum_{i=j}^{3N} q_i F_{i,j} q_j ,$$

where $F_{i,j} \equiv \left.\frac{\partial^2 V}{\partial q_i \partial q_j}\right|_{0,0,\ldots}$ is the mass scaled <u>Force Constant Matrix</u>. In matrix notation

$$\mathbf{q} = \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_{3N} \end{bmatrix}; \quad \mathbf{q}^t = \left[q_1 q_2 \cdots q_{3N} \right]$$

and thus

$$H = \underbrace{\frac{\mathbf{1}}{\mathbf{2}}\dot{\mathbf{q}}^{t}\dot{\mathbf{q}}}_{\mathbf{T}} + \underbrace{\frac{\mathbf{1}}{\mathbf{2}}\mathbf{q}^{t}\mathbf{F}\mathbf{q}}_{\mathbf{V}}$$

<u>Example</u> 3 atoms

$$\mathbf{q} = \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_9 \end{bmatrix}; \quad q_1 = \tilde{x}_1 - \tilde{x}_1^0 \ , \ q_9 = \tilde{z}_3 - \tilde{z}_3^0$$

$$T = \tfrac{1}{2}\left[\dot{q}_1\dot{q}_2 \cdots \dot{q}_9\right] \begin{bmatrix} \dot{q}_1 \\ \dot{q}_2 \\ \vdots \\ \dot{q}_9 \end{bmatrix} = \tfrac{1}{2}\left(\dot{q}_1^2 + \dot{q}_2^2 + \cdots + \dot{q}_9^2\right) \quad ✓$$

$$V = \tfrac{1}{2}\left[q_1 q_2 \cdots q_9\right] \begin{bmatrix} F_{11} & F_{12} & \cdots & F_{12} \\ F_{21} & F_{22} & \cdots & F_{29} \\ \vdots & & & \\ \vdots & & & \\ F_{91} & F_{92} & & F_{99} \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ \vdots \\ q_9 \end{bmatrix} = \tfrac{1}{2}\sum_i \sum_j q_i F_{ij} q_j \quad ✓$$

Note $F_{ij} = F_{ji}$, i.e., **F** is a <u>symmetric matrix</u>

$$\left(\text{"Proof"} \quad \frac{\partial^2 V}{\partial q_i \partial q_j} = \frac{\partial^2 V}{\partial q_j \partial q_i}\right)$$

Also, note

T is separable, i.e., $T = \sum_i t_i$, where $t_i = \tfrac{1}{2}\dot{q}_i^2$,

but V is <u>not</u> separable, i.e., $V = \sum_i V_i$.

Thus, even to lowest (2^{nd}) order there is coupling. However, because V is bilinear in $q_i q_j$ there exists a transformation to a new set of variables, Q_i such that T and V are both separable in the Q_i.

Let $\boldsymbol{q} = \boldsymbol{CQ}$, where $\boldsymbol{C}$ is a 3N x 3N matrix. Consider a special class of matrices called orthogonal matrices. These have the property that

$\boldsymbol{C}^{-1} = \boldsymbol{C}^t$, where $\boldsymbol{C}^t$ is the transpose of $\boldsymbol{C}$.

That is,

$$\left(C^t\right)_{i,j} = C_{j,i}$$

Thus,

$$\boldsymbol{q}^t = \left(\boldsymbol{CQ}\right)^t = \boldsymbol{Q}^t\boldsymbol{C}^t = \boldsymbol{Q}^t\boldsymbol{C}^{-1}$$

Aside—if $D = \boldsymbol{EF}$ then $\boldsymbol{D}^t = \boldsymbol{F}^t\boldsymbol{E}^t$

$$\text{Proof—}D_{ij} = \sum_k E_{ik}F_{kj}, \qquad D_{ij}^t \overset{?}{=} \sum_k F_{ik}^t E_{kj}^t$$

$$= \sum_k F_{ki}E_{kj} = \sum_k E_{jk}F_{ki}$$

$$= D_{ji} \quad ✓$$

Thus,

$$T = \tfrac{1}{2}\dot{\boldsymbol{q}}^t\dot{\boldsymbol{q}} = \tfrac{1}{2}\dot{\boldsymbol{Q}}^t\underbrace{\boldsymbol{C}^t\boldsymbol{C}}_{I}\dot{\boldsymbol{Q}} = \tfrac{1}{2}\dot{\boldsymbol{Q}}^t\dot{\boldsymbol{Q}}$$

$$= \tfrac{1}{2}\sum_i \dot{Q}_i^2 = \sum_i t_i$$

$$V = \tfrac{1}{2}\boldsymbol{q}^t\boldsymbol{F}\boldsymbol{q} = \tfrac{1}{2}\boldsymbol{Q}^t\left(\boldsymbol{C}^t\boldsymbol{F}\boldsymbol{C}\right)\boldsymbol{Q} \equiv \tfrac{1}{2}\boldsymbol{Q}^t\Lambda\boldsymbol{Q}$$

The new force const matrix $\Lambda = \boldsymbol{C}^t \boldsymbol{F} \boldsymbol{C}$ and we determine $\boldsymbol{C}$ by requiring Λ to be <u>diagonal</u>. This is a example of an eigenvalue/eigenvector problem. Before discussing that, what advantage is there in requiring Λ to be diagonal?

Ans: $$H = \sum_i (t_i + V_i) = \sum_i \tfrac{1}{2}\dot{Q}_i^2 + \tfrac{1}{2}\Lambda_i Q_i^2$$

Now the system looks like 3N <u>uncoupled</u> harmonic oscillators with <u>normal mode harmonic </u>frequencies

$$\omega_i = \sqrt{\Lambda_i}\ .$$

Return to $\boldsymbol{C}^t \boldsymbol{F} \boldsymbol{C} = \Lambda$ (diagonal).

Thus, multiply by $\boldsymbol{C}$ to get $\underbrace{\boldsymbol{C}\boldsymbol{C}^t}_{1}\boldsymbol{F}\boldsymbol{C} = \boldsymbol{C}\Lambda$ thus

$$\boxed{\boldsymbol{F}\boldsymbol{C} = \boldsymbol{C}\Lambda}$$

Consider a 2x2 example:

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}\begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix}\begin{pmatrix} \Lambda_1 & 0 \\ 0 & \Lambda_2 \end{pmatrix}$$

Can show (homework) this is equivalent to:

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}\begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix} = \Lambda_1 \begin{pmatrix} C_{11} \\ C_{21} \end{pmatrix} \qquad \text{and}$$

$$\begin{pmatrix} F_{11} & F_{12} \\ F_{21} & F_{22} \end{pmatrix}\begin{pmatrix} C_{12} \\ C_{22} \end{pmatrix} = \Lambda_2 \begin{pmatrix} C_{12} \\ C_{22} \end{pmatrix}$$

Thus,

$$\boldsymbol{FC}^{(1)} = \Lambda_1 \boldsymbol{C}^{(1)}; \qquad \boldsymbol{FC}^{(2)} = \Lambda_2 \boldsymbol{C}^{(2)},$$

where

$\boldsymbol{C}^{(1)}$, $\boldsymbol{C}^{(2)}$, $\cdots \boldsymbol{C}^{(3N)}$ are the <u>columns</u> of the ***C***-matrix. These columns are called the <u>eigenvectors</u>. The procedure to find the ***C***-matrix is termed finding the eigenvalues and eigenvectors of ***F***.

$$\boxed{\boldsymbol{FC} = \boldsymbol{C}\Lambda}$$

(I will spare you the details on how this is "diagonalization of ***F***" is done.)

<u>Remarks</u>

There are 6 zero frequency modes, i.e., $\Lambda_1 - \Lambda_6 = 0$. These normal modes correspond to 3 translations and 3 rigid rotations of the equilibrium system, for which there is the remaining 3N-6 ωs $(\Lambda_{7,-3N-6})$ are not zero and they are the normal mode vibration frequencies.

For each ω_i there is a corresponding eigenvector, $\boldsymbol{C}^{(i)}$ which relates normal mode Q_i to the $q_{j,j=1,\ldots,3N}$, the mass-scaled cartesian displacements. Recall $\boldsymbol{q} = \boldsymbol{CQ}$, so $\boldsymbol{Q} = \boldsymbol{C}^t \boldsymbol{q}$,

$$\begin{bmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_{3N} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{21} & \cdots & C_{N1} \\ C_{12} & C_{22} & & \\ \vdots & & & \\ & & & \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_{3N} \end{bmatrix}$$

$$Q_1 = c_{11} q_1 + c_{21} q_2 + \cdots + c_{N1} q_{3N}$$

To visualize the mode, place a vector on each atom with components (c_{11}, c_{21}, c_{31}), etc.

Equations of motion

$$H_{classical} = \sum_i h_i^c ; \qquad h_i^c = \frac{P_i^2}{2} + \tfrac{1}{2}\omega_i^2 Q_i^2$$

$$Q_i(t) = A\cos\omega_i t + B\sin\omega_i t$$

$$H_{qm} = \sum_i h_i^q ; \qquad h_i^q = -\frac{\hbar^2}{2}\frac{d^2}{dQ_i^2} + \tfrac{1}{2}\omega_i^2 Q_i^2$$

$$\left(h_i^q - \varepsilon_n^{(i)}\right)\varphi_n^{(i)}(Q_i) = 0$$

$$\varepsilon_n^{(i)} = \hbar\omega_i\left(n_i + \tfrac{1}{2}\right);\ n = 0,1,2,\ldots$$

$$E_{total} = \sum_i \hbar\omega_i\left(n_i + \tfrac{1}{2}\right)$$

Total zero-point energy $= \sum_i \hbar\omega_i / 2$

For IR-active mode light is absorbed at fundamental frequencies ω_i^{active}. Also, obtain vibrational partition functions, x-ray structure factors, etc.

II. Examples and practical matters

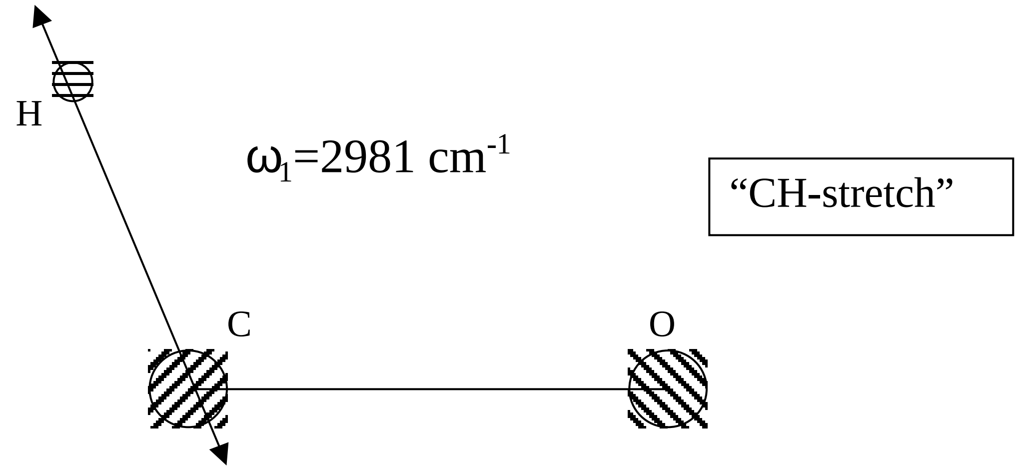
HCO (formyl radical) 3 vibrational. modes. Units: ω is typically reported in spectroscopy as cm^{-1}!! But, ω should be sec^{-1}. Let $\tilde{\omega} = \omega / c$, c

is the speed of light. Then $\tilde{\omega}$ has dimensions of cm^{-1}. Notation should be $\tilde{\omega}$ but people get lazy and just use ω. What about $\hbar\omega\left(n+\frac{1}{2}\right)$? This is an energy. How to convert from $\tilde{\omega}\left(\mathrm{cm}^{-1}\right)$ to energy.

1 hartree	219474.6 cm-1

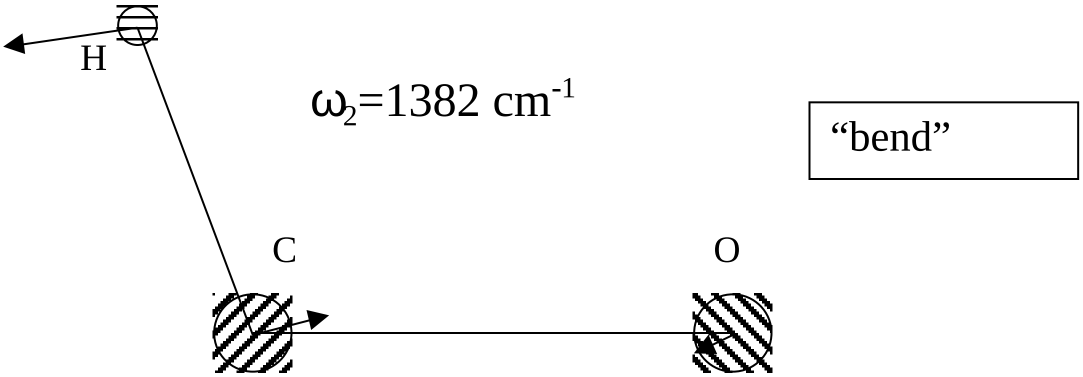
What about ***V***? This was obtained by saving the electronic energy as a function of nuclear geometry. A search for the minimum was successful and the force constant matrix was obtained numerically.

HCO Normal Modes



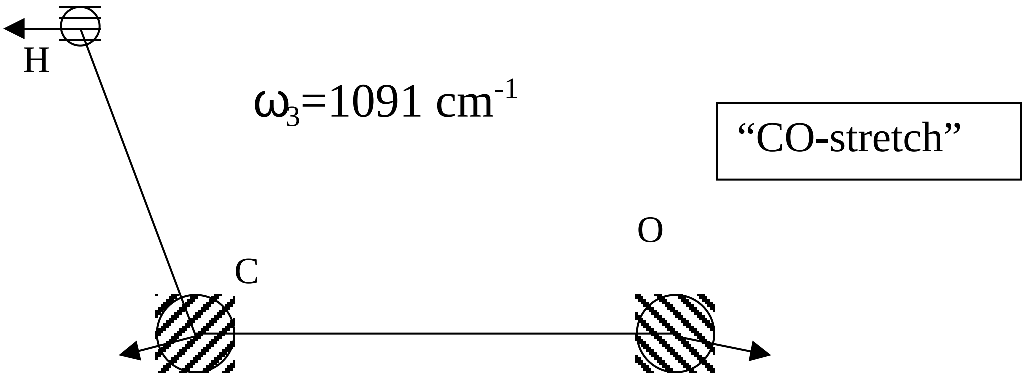
$\omega_1 = 2981\ \mathrm{cm}^{-1}$

“CH-stretch”



$\omega_2 = 1382\ \mathrm{cm}^{-1}$

“bend”



$\omega_3 = 1091\ \mathrm{cm}^{-1}$

“CO-stretch”

Si(100)—2x1 cluster (28 atoms), 2 layers. The vibrational modes of an ordered solid are termed phonons. The potential in this example was a model one based on harmonic nearest neighbor and next nearest neighbor interactions.

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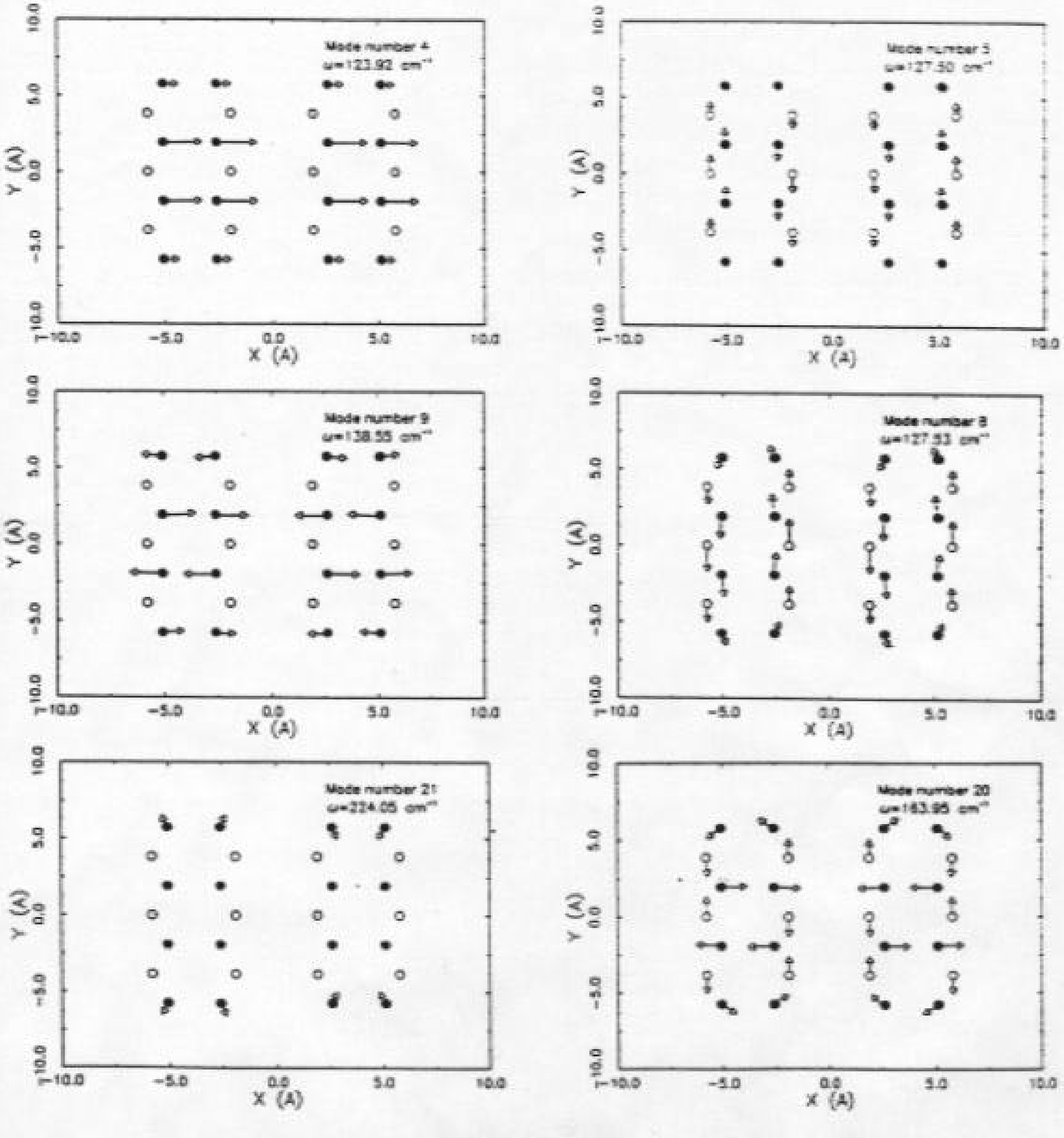

FIG. 3. Six normal modes for Si(100)-(2×1) in the xy plane. Closed circles (●) are the first-layer atoms and open circles (○) are the second-layer atoms.

III. What about <u>anharmonicity</u> and <u>coupling</u>

Anharmonicity

$$\underbrace{V_i\left(Q_i\right) = \tfrac{1}{2}\omega_i^2 Q_i^2 +}_{\boxed{\text{anharmonic terms}}} c_i Q_i^3 + d_i Q_i^4 + \cdots$$

All potentials contain such terms; however, for very small amplitude motion they may be very small. “Easy” to treat anharmonic terms.

Coupling

$$V\left(Q_1, Q_2, \cdots\right) = \sum_i V_i\left(Q_i\right) + aQ_1Q_2^2 + bQ_iQ_2^3Q_4 + \cdots$$

<u>Coupling</u> terms in $V\left(Q_1, Q_2, \cdots, Q_{3N-3}\right)$ are terms that involve two or more modes. This is hard to treat, but very important to consider. For example, $H_2O \rightarrow OH + H$ <u>must</u> involve coupling.

The importance of anharmonicity and coupling
In HCO (energies in cm^{-1})

	NMHO	NMAO	NMAO/C	EXP
ZPE	2899	2857	2836	
ν_1	1145	1147	1104	1087
ν_2	1905	1869	1885	1868
ν_3	2748	2494	2448	2435

Conclusion: NMHO is qualitatively correct, but not quantitative. (Huge CH(ν_3) stretch anharmonicity.)