Quantum Calculations: CHEM 870/353

Vibrational modes

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Outline

Vibrational modes and Spectroscopy

Why do we care?
Spectroscopy is how we identify atoms and molecules.
The energy of transitions between vibrational modes are the
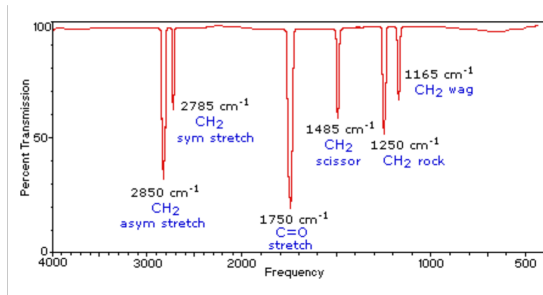FINGERPRINT of the molecule.

Figure: The infrared (IR) spectrum of formaldehyde, $CH_2=O$

Note: the energies are given in wavenumbers, cm^{-1}.

Normal Modes - mathematical background

Polyatomic Molecules Vibrate

To describe a molecule with N atoms, one needs $3N$ coordinates:

$$\{x_n, y_n, z_n\}$$

A molecule has $3N$ degrees of freedom (DOF), as each coordinate is free to move idependently.

$$N \equiv N_{(x_2, y_2, z_2)}$$

$$(x_1, y_1, z_1)$$

We can re-assign the DOF to better describe vibrations (and rotations).

Normal Modes and Degrees of Freedom

> **There are more vibrational modes for linear molecules.**
> - Re-assign the DOF to count number of vibrational modes.
> - Three coordinates are used to define the center of mass (COM) and its translational motion.
> - Two (linear) or three (nonlinear) coordinates are used to define rotational motion.
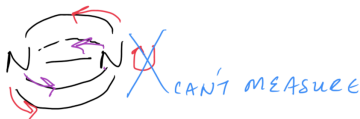> - The 'left-over' DOF are assigned to vibrational modes.

DOF	Linear	Nonlinear
translational	3	3
rotational	2	3
vibrational	$3N-5$	$3N-6$

Linear molecules only rotate about 2 axes.

Normal Mode of the nitrogen diatomic molecule

DOF	Linear	Nonlinear
translational	3	3
rotational	2	3
vibrational	$3N-5$	$3N-6$

CAN'T MEASURE

Linear molecules only rotate about 2 axes.

Nitrogen's stretching mode

For N_2, $N = 2$ so the vibrational DOF are:

$$3N - 5 = 3(2) - 5 = 1$$

There is only one vibrational mode!

STRETCHING MODE

Each Normal Mode has a Fundametal Frequency

For Harmonic Oscillators, the levels are equally spaced

Consider the transition from n to $n+1$

$$\Delta E = h\nu_{\text{obs}} = E_{n+1} - E_n$$

$$\nu_{\text{obs}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}(\text{Hz})$$

Change to wavenumbers:

$$G_{i,n} = \tilde{\omega}_i\left(n + \frac{1}{2}\right) = \frac{E_n}{hc}$$

Remember: Only one energy is needed to identify this vibrational mode!

Each Normal Mode has a Fundametal Frequency

A molecule with three atoms has three modes: $3N-6=3$

Each mode has a different fundametal frequency and thus a characteristic wavenumber.

$$G_{i,n} = \tilde{\omega}_i(n + \tfrac{1}{2})$$

$$\tilde{\omega}_i = \frac{1}{2\pi c}\sqrt{\frac{k_i}{\mu_i}}$$

With anharmonicity:

$$G_{i,n} = \tilde{\omega}_i(n + \tfrac{1}{2}) + \tilde{x}_i\tilde{\omega}_i(n + \tfrac{1}{2})^2$$

Comes from Taylor Expansion of Harmonic Potential:

$$V(l) = V(l_0) + \left(\frac{\partial V}{\partial l}\right)_{l=l_0}(l - l_0) + \frac{1}{2!}\left(\frac{\partial^2 V}{\partial l^2}\right)_{l=l_0}(l - l_0)^2 + ...$$

Each Normal Mode has a Fundametal Frequency

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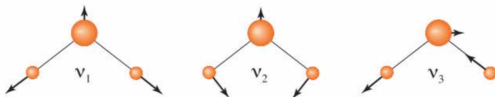
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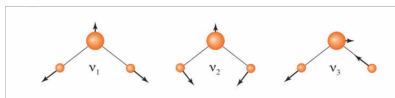
Normal Coordinates for the Hamiltonian

The Potential Energy term is now:

$$V(\{Q_j\}) = \frac{1}{2} \sum_{j=1}^{N_{\text{vib}}} F_j Q_j^2$$

Q_j are the normal coordinates (for each j mode)
N_{vib} is the number of vibrational DOF (modes).
F_j is related to the restoring Force of the mode.

The Hamiltonian is now (Kinetic + Potential) :

$$\hat{H}_{\text{vib}} = - \sum_{j=1}^{N_{\text{vib}}} \frac{\hbar^2}{2\mu_j} \frac{\partial^2}{\partial Q_j^2} + \frac{1}{2} \sum_{j=1}^{N_{\text{vib}}} F_j Q_j^2$$

The Zero Point Energy of Each Mode

Each vibrational mode has a ground state (n=0)

The total energy due to vibrations is:

$$E_{\text{vib}} = \sum_{j=1}^{N_{\text{vib}}} h\nu_j(n_j + \tfrac{1}{2})$$

These energies were found using *separation of variables*:

$$\Psi_{\text{vib}}(Q_1, Q_2, ..., Q_N) = \psi_{\text{vib1}}(Q_1)\psi_{\text{vib2}}(Q_2)...\psi_{\text{vibN}}(Q_N)$$

- Each vibrational mode also has excited states.
- Usually we measure the fundamental transition (n=0 to n=1) to identify the mode.
- High energy, random seeming vibrations of the molecule can be decomposed into these vibrational modes.

Infrared and Raman Spectroscopy

The vibrational mode must couple to the electromagnetic field

The transition dipole moment is:

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i \, d\tau$$

Where the transition dipole moment operators is:

$$\hat{\mu} = \sum_i Q_i \vec{r_i}$$

where $\vec{r_i}$ is the displacement of charge Q_i from the origin.

- If μ_{fi} is non-zero, the transition is allowed. Otherwise it is 'forbidden', though there are many exceptions.
- The above equations hold for electronic, vibrational, and rotational transitions.
- Each type of transition has it's own selection rules.

Infrared and Raman Selection Rules

Infrared requires dipole moments

The molecule must have a dipole moment or the vibrational mode must create a dipole moment.

$$\overset{\longleftarrow}{O} = C = \overset{\longrightarrow}{O} \qquad\qquad \overset{\longrightarrow}{O} = \overset{\longleftarrow}{C} = \overset{\longrightarrow}{O}$$

A   B

Raman requires polarizability

Raman requires that the polarizability changes as the molecule vibrates. Now write the transition dipole moment operators as:

$$\hat{\mu} = \alpha(x)E(t)$$

where $\alpha(x)$ is the polarizability of the molecule and $E(t)$ is the electromagnetic field.

Infrared and Raman Exclusion Rule

For Polyatomic molecules

If a molecule has a center of symmetry, then no modes can be both infrared AND Raman active. Note, a mode can be inactive in both.

Which of the modes above is Raman active?
Which is IR active?