THE VIBRATIONAL SPECTRUM

Selection Rules. The most intense transitions are induced by the E field of the radiation interacting with the electric dipole of the molecule. We'll show when we study perturbation theory that the intensity of such a transition is proportional to the square of the transition dipole moment,

\[ \langle \psi_i | \mu | \psi_f \rangle. \]

\[ \psi_i \quad \psi_f \]

Fig. 11.1. The transition dipole for \( \psi_i \rightarrow \psi_f \).

Here \( \mu \) is the dipole moment of the molecule at the bond length of the initial state, and \( |\psi_i\rangle = |v\rangle \), \( |\psi_f\rangle = |v'\rangle \) (since we're changing vibrational state). So we want to calculate

\[ \langle v' | \mu | v \rangle \]

We can expand the dipole moment as a Taylor series about its value at the equilibrium bond length

\[ \mu = \mu_0 + \left( \frac{d\mu}{dg} \right)_0 \xi + \ldots \]

\( \mu_0 \) = dipole moment when displacement \( \xi \) is zero.
To a reasonable approximation we can ignore higher order terms, since the dipole is approximately linear in the displacement. (In fact in a purely ionic system it's exactly linear! Deviations are caused by rearrangements of charge when the bond length changes.)

\[ \mu = \mu_0 + (d\mu/d\xi)_0 \xi \]

Fig. 11.16. The dependence of electric dipole moment on bond length.

\[ \langle \nu', \mu_0 \mid \nu \rangle = \langle \nu', \mu_0 \mid \nu \rangle + \langle \nu', \mu_0 \mid \frac{\partial \mu}{\partial \xi} \rangle \xi \mid \nu \rangle \]

\[ = \mu_0 \langle \nu', \mu_0 \mid \nu \rangle + \left( \frac{\partial \mu}{\partial \xi} \right)_0 \langle \nu', \xi \mid \nu \rangle \]

0, by orthogonality of \( |\nu'\rangle, |\nu\rangle \) (\( \frac{\partial \mu}{\partial \xi} \)) \( \neq 0 \)!

\( \therefore \) In order for a molecule to show vibrational transitions, its dipole moment must change with displacement! (Homonuclear diatomics, e.g., H\(_2\), Cl\(_2\) don't show a vibrational spectrum.)
Note that the harmonic approximation predicts only one line in the spectrum, at energy, \( E = E_{v+1} - E_v = \hbar \omega \) 

This is not entirely true! There are 2 sources of anharmonicity:

1. Mechanical Anharmonicity
   - Typical real potential
   - Less confining as \( E \uparrow \):
     - energy levels converge (become "less quantized") as \( E \uparrow \)
   - Also U's change from those of a H.O.: selection rules are relaxed and transitions with \( \Delta v = \pm 2, \pm 3, \ldots \) appear in spectrum.

Fig. 11.17. The harmonic approximation and the actual molecular potential energy.

2. Electrical Anharmonicity: \( \mu \) may have terms \( \propto \xi^2, \xi^3 \) etc. Then transitions corresponding to \( \Delta v = 2, 3 \) etc. (overtones) are allowed.
An Example: \( \text{CO}_2 \)

\( \text{not normal modes} \)

\( \text{symmetric normal mode} \)

\( \text{anti-symmetric normal mode} \)

\( \text{translation} \)

\( \text{vibration in 1 bond} \)

\( \text{vibration in the other bond} \)

\[ Q_1 = \frac{1}{\sqrt{2}} \left( q_1 - q_3 \right), \quad K_1 = \frac{k}{M_0} \]

\[ Q_2 = \frac{1}{\sqrt{2M}} \left( \sqrt{M_0} q_1 - 2 \sqrt{M_0} q_2 + \sqrt{M_0} q_3 \right), \quad K_2 = \frac{kM}{M_0 M_1} \]

\[ Q_3 = \frac{1}{M} \left( M_1 q_1 - \sqrt{M_0} q_2 + \sqrt{M_0} q_3 \right), \quad K_3 = 0 \]

\( M = \text{total mass of molecule} = M_0 + 2M_1 \)

Fig. 11.21. (a) and (b) show two of the bond vibrations; (c) and (d) show two of their linear combinations corresponding to normal modes; (e) is a translational displacement.

Note that relative masses determine form of normal coordinates (via the effective force constants, \( k \)).