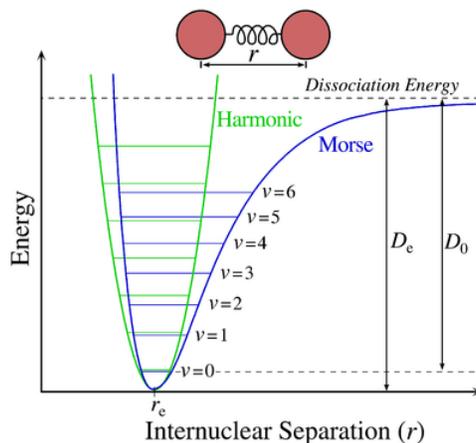


12.13: Symmetry of Vibrations Describes their Spectroscopic Behavior

Vibrational transitions in molecules

The potential energy surface (electronic state), often approximated as a Morse potential, describes the energy of the eigenstate as a function of the interatomic distance. When an electron is excited from one eigenstate to another within the electronic state there is a change in interatomic distance, this results in a vibration occurring.



Vibrational transitions often occur when a molecule absorbs or emits infrared light, though, as we will see later, there are other processes that can cause vibrational transitions. During the vibrational transition, the electrons remain in the same electronic state, but that vibrational state changes from one eigenstate to another. In the case of the Morse diagram above, the vibrational eigenstates are denoted as ν . As you can see from the diagram the eigenstate is a function of energy versus interatomic distance. To predict whether a vibrational transition will occur, or for that matter a transition of any kind, we use the transition moment integral:

$$\int \Psi_i^* \mu \Psi_f d\tau = \langle \Psi_i | \mu | \Psi_f \rangle$$

The transition moment integral is written here in standard integral format, but this is equivalent to Bra & Ket format which is standard in most chemistry quantum mechanical text (The $\langle \Psi_i |$ is the Bra portion, $|\Psi_f \rangle$ is the Ket portion). The transition moment operator μ is the operator that couples the initial state Ψ_i to the final state Ψ_f , which is derived from the time independent Schrödinger equation. However using group theory we can ignore the detailed mathematical methods. We can use the Γ_{ir} of the vibrational energy levels and the symmetry of the transition moment operator to find out if the transition is allowed by selection rules. The selection rules for vibrations or any transition is that it is allowed, for it to be allowed by group theory the answer **must contain the totally symmetric Γ_{ir}** , which is always the first Γ_{ir} in the character table for the molecule in question.

Infrared Spectroscopy

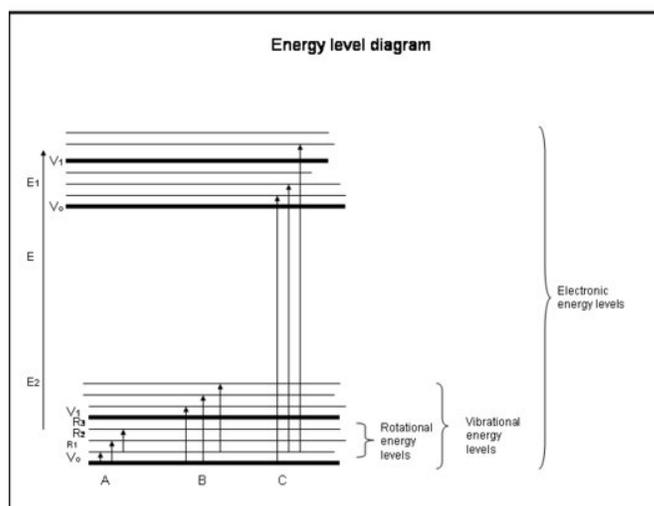
Infrared Spectroscopy (IR) measures the vibrations that occur within a single electronic state, such as the one shown above. Because the transition occurs within a single electronic state there is a variation in interatomic distance. The dipole moment is dictated by the equation.

$$\vec{\mu} = \alpha \vec{E}$$

Where $\vec{\mu}$ is the magnitude of dipole moment; α is the polarizability constant (actually a tensor) & E is the magnitude of the electric field which can be described as the electronegativity.³ Therefore when a vibration occurs within a single electronic state there is a change in the dipole moment, which is the definition of an active IR transition.

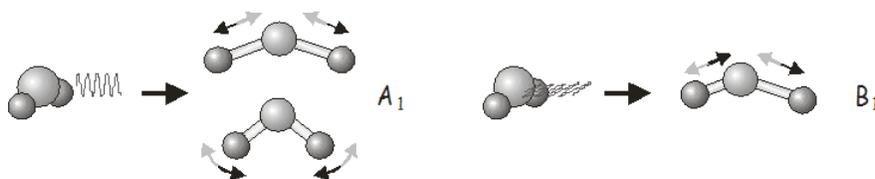
$$\left(\frac{d\mu}{dq} \right)_{eq} \neq 0$$

In terms of group theory a change in the dipole is a change from one vibrational state to another, as shown by the equation above. A picture of the vibrational states with respect to the rotational states and electronic states is given below. In IR spectroscopy the transition occurs only from one vibrational state to another all within the same electronic state, shown below as B.



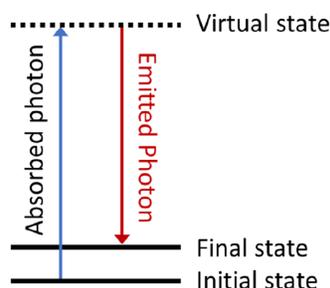
Light polarized along the x , y , and z axes of the molecule may be used to excite vibrations with the same symmetry as the x , y and z functions listed in the character table.

For example, in the C_{2v} point group, x -polarized light (light polarized in the x direction) may be used to excite vibrations of B_1 symmetry, y -polarized light to excite vibrations of B_2 symmetry, and z -polarized light to excite vibrations of A_1 symmetry. In H_2O , we would use z -polarized light to excite the symmetric stretch and bending modes, and x -polarized light to excite the asymmetric stretch. Shining y -polarized light onto a molecule of H_2O would not excite any vibrational motion.



Raman Scattering

If there are vibrational modes in the molecule that may not be accessed using a single photon, it may still be possible to excite them using a two-photon process known as Raman scattering. An energy level diagram for Raman scattering is shown below.



The first photon excites the molecule to some high-lying intermediate state, known as a *virtual state*. Virtual states are not true stationary states of the molecule (i.e. they are not eigenfunctions of the molecular Hamiltonian), but they can be thought of as stationary states of the 'photon + molecule' system. These types of states are extremely short lived, and will quickly emit a photon to return the system to a stable molecular state, which may be different from the original state. Since there are two photons (one absorbed and one emitted) involved in Raman scattering, which may have different polarizations, the transition dipole for a Raman transition transforms as one of the Cartesian products x^2 , y^2 , z^2 , xy , xz , yz listed in the character tables.

Vibrational modes that transform as one of the Cartesian products may be excited by a Raman transition, in much the same way as modes that transform as x , y , or z may be excited by a **one-photon** vibrational transition.

In H_2O , all of the vibrational modes are accessible by ordinary one-photon vibrational transitions. However, they may also be accessed by Raman transitions. The Cartesian products transform as follows in the C_{2v} point group.

$$\begin{array}{ll} A_1 & x^2, y^2, z^2 \\ A_2 & xy \end{array} \quad \begin{array}{ll} B_1 & xz \\ B_2 & yz \end{array} \quad (27.5)$$

The symmetric stretch and the bending vibration of water, both of A_1 symmetry, may therefore be excited by any Raman scattering process involving two photons of the same polarization (x -, y - or z -polarized). The asymmetric stretch, which has B_1 symmetry, may be excited in a Raman process in which one photon is x -polarized and the other z -polarized.

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