

3.6: IR and Raman Activity

Selection Rule for IR

Recall, that for IR activity, we require that

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

If motion along the normal coordinate does not change the dipole moment, the transition is forbidden. In order for μ to be changed by the normal coordinate, at least one of the following must be non-zero!

$$\langle v=0 | \hat{x} | v \neq 0 \rangle$$

$$\langle v=0 | \hat{y} | v \neq 0 \rangle$$

$$\langle v=0 | \hat{z} | v \neq 0 \rangle$$

integrated over q , the normal coordinate. **This is since μ is a vector that transforms as x, y, z in the point group.** The polarization of the IR transition is determined by which transition integral is *non-zero*. This is very much like the criterion for an electronically allowed transition.

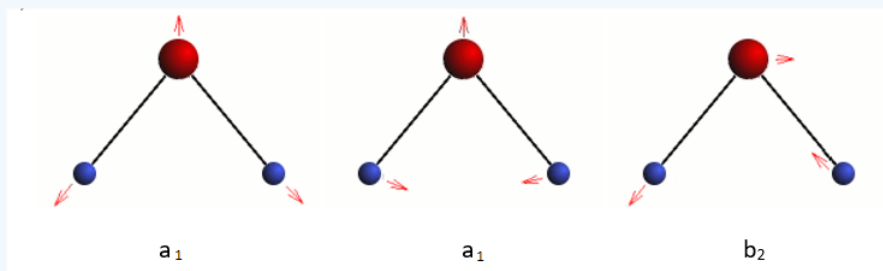
All $|v=0\rangle$ are a_1 (totally symmetric) and $|v=1\rangle$ has the same symmetry as the singly excited normal mode, q . Since

$$A_1 \otimes \Gamma_{x,y,z} \otimes \Gamma_q \supset A_1$$

The transition will be IR active if the normal mode symmetry belongs to the same irreducible representation as x, y , or z for the point group of the molecule. This can be applied immediately to H_2O .

✓ Example 3.6.1: Water

Water has three vibrational modes.



Three normal modes of water

Whether any of these modes is active in the infrared region of the spectrum is the question. This is determined by evaluating the quantum mechanical transition probability integral,

$$P = e \int \Psi^f(vib) \hat{q} \Psi^i(vib) d\tau$$

where q is the spatial coordinate and is either x, y , or z . If this integral is non-zero the transition is allowed. Group theory enables us to determine if the integral is non-zero as follows. We evaluate the direct product (note the similarity to the quantum mechanical transition probability integral) $\Gamma_{vib}^f \Gamma_q \Gamma_{vib}^i$ and if it turns out to be equal to, or contain, the irreducible representation A_1 then the transition is allowed. If the direct product isn't equal to or contain A_1 then the transition is forbidden.

Γ_{vib}^i , the representation for the ground state is always equal to A_1 and Γ_{vib}^f is always equal to A_1 and Γ_{vib}^f has the symmetry of the vibrational mode being excited, which in our case is either A_1 or B_2 . Thus we can see that a vibrational mode will be infrared active if it belongs to the same symmetry species as one of the Cartesian coordinates. You should verify that this is correct and also be able to show that all three vibrational modes of the water molecule are infrared active.

Selection Rule for Raman

Recall, for Raman activity, there must be a change in the polarizability with respect to the normal mode.

The components of the polarizability transform as the quadratic functions of x, y, z , i.e. $x^2, y^2, z^2, xy, xz, yz$ or combinations thereof (x^2-y^2). Thus we require that for the polarizability operator to transform as one of the quadratic terms e.g.

with

Thus since has the same symmetry as the singly excited normal mode, q . The transition integrals we know and love will be:

for at least one representation of polarization. At least one quadratic form transforms as each one of the irreducible representations. Therefore, all possible vibrations of any C_{2v} molecule will be Raman allowed. But what about other point groups?

Centrosymmetric molecules – exclusion rules

There are important examples for which the IR allowed and Raman allowed transitions are mutually exclusive. There are molecules having a center of inversion. In this case, their normal coordinates, q , must be either g or u , depending on their behavior toward the \hat{i} operation. Thus $|v=1\rangle$ must be either g or u , while $|v=0\rangle$ will always be g .

In centrosymmetric molecules, the x, y, z operators are u -operators, while all components of \hat{P} are g -operators (go look it up on the O_h point group character table!) i.e.

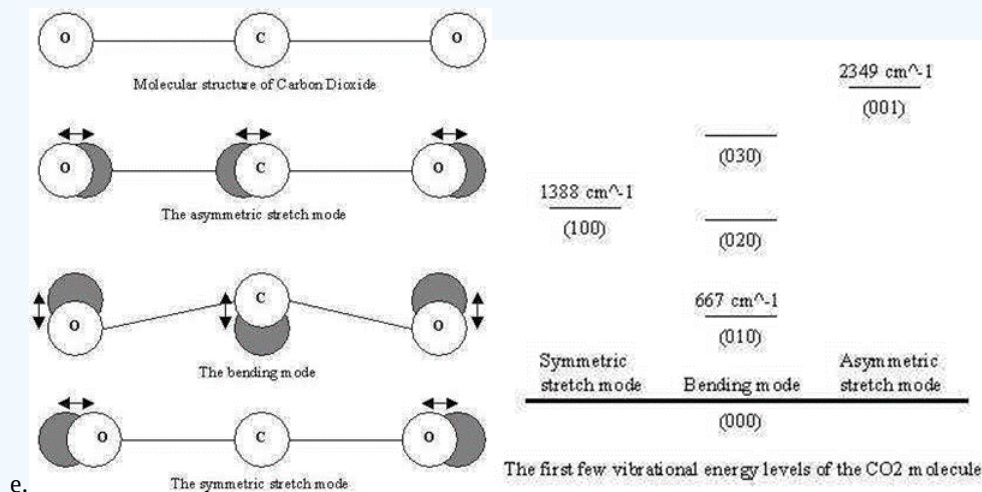
$$\hat{x}^2 = (-x)^2 \quad \therefore g \text{ symmetry}$$

$$\hat{x} = -(-x) \quad \therefore u \text{ symmetry}$$

This symmetry behavior leads to the rule for centrosymmetric molecules. Excitation of g -normal modes are forbidden in the IR, while excitation of u -normal modes are forbidden in Raman.

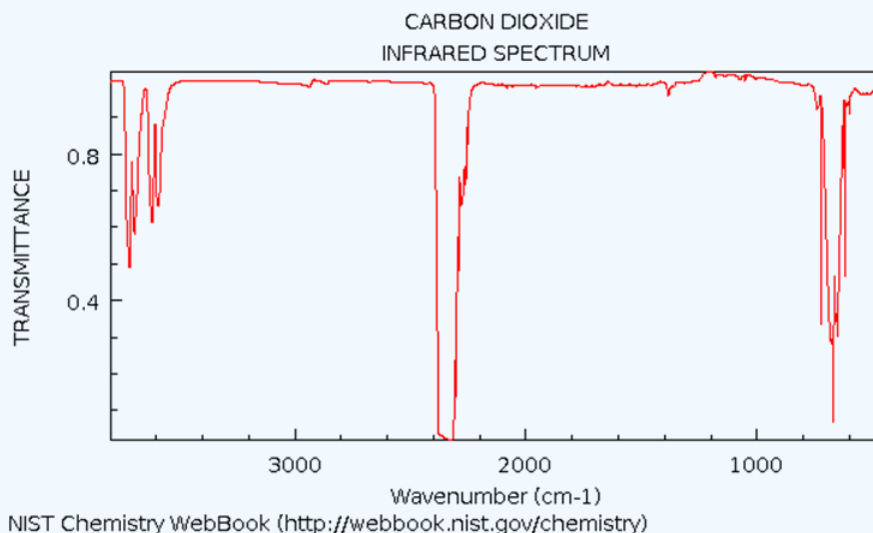
✓ Example 3.6.1

Carbon Dioxide is a linear triatomic molecule with $3N-5=4$ normal modes:



The point group is $D_{\infty h}$ and the irreducible representations are Σ_g^+ , Σ_u^+ , and Π_u respectively. Thus only asymmetric stretch and bends are found in the IR, while only the symmetric stretch is found in Raman spectra.

The IR spectrum of CO₂ (4.0 kPa total pressure) is shown below. Note these extra bands: $\nu_3 + \nu_1 = 3610 \text{ cm}^{-1}$ and $\nu_3 + 2\nu_2 = 3710 \text{ cm}^{-1}$



Vibrational frequency nomenclature

The $3N - 5$ (5) fundamental frequencies are usually numbered sequentially, $\nu_1, \nu_2, \nu_3, \dots, \nu_{3N-6}$. The convention is that the highest frequencies of totally symmetric vibrations in ν_1 follow all other totally symmetric vibrations in order of *decreasing* frequency. Once all totally symmetric vibrations are numbered, the next number goes to the highest frequency non-symmetric vibration.

For H_2O :

- ν_1 is the "symmetric stretch"
- ν_2 is the "asymmetric stretch"
- ν_3 is the "symmetric bend"

Exception, the bending mode of a linear molecule is ν_2

For CO_2 :

- ν_1 is the "symmetric stretch"
- ν_2 is the "symmetric bend"
- ν_3 is the "asymmetric stretch"

If IR and Raman spectra consisted only of fundamental and overtones, spectra would be easier to assign, but combinations bands, $\nu_1 \pm \nu_2$ and overtones $2\nu_1$ also appear, complicating the assignment of the fundamental frequencies.

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