

# Spectroscopy

## Exercises Chapter 4A

1. In class I have shown that for transitions within the same electronic state of a diatomic molecule, the selection rules are determined by evaluating the following transition moment integral:

$$\int \psi_{2vib}^*(R) \hat{\mu}(R) \psi_{1vib}(R) d\tau_R \int \psi_{2rot}^*(\theta, \varphi) \cos \theta \psi_{1rot}(\theta, \varphi) d\tau_{\theta, \varphi}$$

This expression must be non-zero for transitions to occur. The first integral determines the vibrational selection rules and the second the rotational selection rules.

Let us for now only consider the vibrational part. To do this integral, one can express the dipole moment operator as a power series in the displacement  $x$

$$\mu = \mu_e + \frac{d\mu}{dx} \bigg|_{x=0} x + \frac{1}{2} \frac{d^2\mu}{dx^2} \bigg|_{x=0} x^2 + \dots$$

To a first approximation, we assumed that the dipole moment function is linear in  $x$  (i.e., neglect the terms of order  $x^2$  and higher).

We then had to evaluate the integral:

$$\int \psi_v^*(x) x \psi_v(x) dx$$

Using harmonic oscillator wave functions and raising and lowering operators we evaluated this integral and determine the  $\Delta v = \pm 1$  selection rules for vibrational transitions.

In practice, these selection rules may be violated when approximations that we have made in our treatment break down.

- Examine the effect of a breakdown in the assumption that the dipole moment is linear in  $x$ . Assume now that in addition to the linear term, there is a term that looks like:

$$\frac{d^2\mu}{dx^2} \bigg|_{x=0} x^2$$

What will be the possible changes in quantum numbers when you use a dipole function which includes this term to evaluate the transition moment integral?

The other thing we have assumed is that the wave functions are well approximated by harmonic oscillator wave functions. This results from neglecting all terms higher than  $x^2$  in the potential  $U(x)$ . This part of the problem explores the breakdown in the harmonic oscillator selection rules due to an additional anharmonic term in the potential.

The effect of higher order terms in the potential can be treated by perturbation theory.

Assume that the vibrational potential for an anharmonic oscillator is:

$$U(x) = \frac{1}{2} k x^2 + \frac{1}{24} b x^4$$

b. Write the  $x^4$  term in terms of raising and lowering operators. You should get 16 different terms in this expression.

Remember that in general, the wave function corrected to first order by perturbation theory is given by:

$$\psi_n = \psi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

The integrals  $H'_{mn}$  are fairly easy to evaluate using raising and lowering operators.

c. Assume that one is interested in selection rules for vibrational transitions out of the  $v=0$  state of the anharmonic oscillator with the potential given above.

By looking at your expression for  $x^4$  in terms of raising and lowering operators, determine which zeroth order functions will contribute to the above summation (which  $H'_{mn}$  will be non-zero). You don't need to find the expansion coefficients, since I am only asking for a qualitative answer to this problem.

d. For what possible values of the change in vibrational quantum number will the transition moment integral be non-zero assuming that the dipole moment function is linear in x?