



Spectroscopy Exercises

Solutions to Exercise 4A

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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:

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

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 :

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

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:

$$\int \Psi_{v'}^* \hat{x} \Psi_{v''} dx$$

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.

a. 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:

$$\left. \frac{d^2\mu}{dx^2} \right|_{x=0} x^2$$

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?

b. 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:

$$U'(x) = \frac{1}{2} kx^2 + \frac{1}{24} bx^4$$

Write the \hat{x}^4 term in terms of raising and lowering operators. You should get 16 different terms in this expression.

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

$$\Psi_n = \Psi_n^{(0)} + \sum \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)}$$

The integrals H_{mn} are fairly easy to evaluate using raising and lowering operators. 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 nonzero). 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 ?

a) In order to evaluate the integrals, the \hat{x} operator is expressed in terms of ladder operators \hat{a}^\dagger , \hat{a} and the integrals evaluated. Note that the term $\frac{d^2\mu}{dx^2}\bigg|_{x=0}$ is merely a constant and can be pulled in front of the integral - thereby not affecting the outcome of the selection rules. For the sake of simplicity, this term is omitted in the following derivation:

$$\begin{aligned}
 \int \Psi_{v'}^* \hat{x}^2 \Psi_{v''} dx &= \langle v' | \hat{x}^2 | v'' \rangle \\
 &= \underbrace{\frac{1}{4\alpha^2}}_{\rho^2} \langle v' | (\hat{a} + \hat{a}^\dagger)^2 | v'' \rangle \\
 &= \rho^2 (\hat{a}^\dagger \hat{a}^\dagger + \underbrace{\hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger}_{=1+2\hat{N}} + \hat{a} \hat{a}) \\
 &= \rho^2 \left[\sqrt{(v_1+1)(v_2+2)} \langle v_2 | v_1+2 \rangle + \langle v_2 | v_1 \rangle + 2v_1 \langle v_2 | v_1 \rangle + \right. \\
 &\quad \left. + \sqrt{v_1(v_1-1)}(1-\delta_{0,v_1})(1-\delta_{0,v_1-1}) \langle v_2 | v_1-2 \rangle \right] \\
 &= \rho^2 \left[\sqrt{(v_1+1)(v_2+2)} \underbrace{\delta_{v_2, v_1+2}}_{\Delta v=2} + (1+2v_1)\delta_{v_1, v_2} + \right. \\
 &\quad \left. + \sqrt{v_1(v_1-1)}(1-\delta_{0,v_1})(1-\delta_{0,v_1-1}) \underbrace{\delta_{v_2, v_1-2}}_{\Delta v=-2} \right]
 \end{aligned}$$

So additionally to the $\Delta v = \pm 1$, the second order term allows $\Delta v = \pm 2$.

b) The \hat{x}^4 expressed as \hat{a}^\dagger and \hat{a} operators can be expanded as follows to give 16 terms (note: in principal one receives terms containing all possible sequences of \hat{a}^\dagger and \hat{a}):

$$\begin{aligned} \hat{x}^4 = \rho^4 & \left(\hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger + \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger \hat{a} + \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a} \hat{a}^\dagger \hat{a}^\dagger + \hat{a} \hat{a}^\dagger \hat{a}^\dagger \hat{a}^\dagger + \hat{a}^\dagger \hat{a}^\dagger \hat{a} \hat{a} + \right. \\ & + \hat{a}^\dagger \hat{a} \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger \hat{a}^\dagger \hat{a} + \hat{a} \hat{a} \hat{a}^\dagger + \hat{a} \hat{a} \hat{a}^\dagger + \hat{a} \hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger \hat{a} + \\ & \left. + \hat{a}^\dagger \hat{a} \hat{a} \hat{a} + \hat{a} \hat{a} \hat{a}^\dagger \hat{a}^\dagger + \hat{a} \hat{a}^\dagger \hat{a} \hat{a}^\dagger + \hat{a}^\dagger \hat{a} \hat{a} \hat{a}^\dagger \right) \end{aligned}$$

c) Elements of the matrix element H_{mn} are proportional to integrals of the type:

$$\int \psi_m^{*(0)} \hat{x}^2 \psi^{(0)}$$

Integrands in which, when reading from right, at any point contain more \hat{a} than \hat{a}^\dagger will vanish due to the ladder-operator rules. With that, the following terms remain:

$$\hat{a}^{\dagger 4} \quad \hat{a}^{\dagger 2} \hat{a} \hat{a}^\dagger \quad \hat{a}^\dagger \hat{a} \hat{a}^{\dagger 2} \quad \hat{a} \hat{a}^{\dagger 3} \quad \hat{a}^2 \hat{a}^{\dagger 2}$$

The first four terms involve transitions from the ground state wavefunction $\psi_0^{*(0)}$ to $\psi_4^{*(0)}$, $\psi_2^{*(0)}$, $\psi_2^{*(0)}$ and $\psi_2^{*(0)}$ respectively. Despite not being 0, the fifth term does not contribute, since it is not part of the summation (for the summation $m \neq n$). Therefore, one has $\psi_4^{*(0)}$, $\psi_2^{*(0)}$, $\psi_0^{*(0)}$, as the zeroth order wavefunctions contributing to the summation.

d) Deriving selection rules for the general case of $v = n$ (as compared to c. where $v = 0$), gives $\psi_n^{*(0)}$, $\psi_{n+2}^{*(0)}$, $\psi_{n-2}^{*(0)}$, $\psi_{n+4}^{*(0)}$ and $\psi_{n-4}^{*(0)}$ as the zeroth order wavefunctions contributing to the summation in H_{mn} . This leads to the following linear combination for the wave-function:

$$|n\rangle = c_{n+4} |n+4\rangle^{(0)} + c_{n+2} |n+2\rangle^{(0)} + c_n |n\rangle^{(0)} + c_{n-2} |n-2\rangle^{(0)} + c_{n-4} |n-4\rangle^{(0)}$$

In analogy to a., the integral is constructed and \hat{x} expressed in terms of \hat{a}^\dagger and \hat{a} :

$$\begin{aligned} \int dx \psi_m^* \hat{x} \psi_n &= \rho \int dx \psi_m^* (\hat{a}^\dagger + \hat{a}) \psi_n \\ &= \rho \int dx \left(c_{m+4} \langle m+4|^{(0)} + c_{m+2} \langle m+2|^{(0)} + c_m \langle m|^{(0)} + c_{m-2} \langle m-2|^{(0)} + \right. \\ &\quad \left. + c_{m-4} \langle m-4|^{(0)} \right) (\hat{a}^\dagger + \hat{a}) \left(c_{n+4} |n+4\rangle^{(0)} + c_{n+2} |n+2\rangle^{(0)} + c_n |n\rangle^{(0)} + \right. \\ &\quad \left. + c_{n-2} |n-2\rangle^{(0)} + c_{n-4} |n-4\rangle^{(0)} \right) \end{aligned}$$

Upon close inspection, one observes that upon expansion of the integrand into its 32 summands (and considering the ladder operator rules) the following bra-ket terms are produced:

$$\begin{aligned} &\langle m+4|n-5\rangle, \langle m+4|n-3\rangle, \dots, \langle m+4|n+3\rangle, \langle m+4|n+5\rangle \\ &\langle m+2|n-5\rangle, \langle m+2|n-3\rangle, \dots, \langle m+2|n+3\rangle, \langle m+2|n+5\rangle \end{aligned}$$

Leading finally
set of selection

$$\begin{aligned} &\vdots \\ &\langle m-4|n-5\rangle, \langle m-4|n-3\rangle, \dots, \langle m-4|n+3\rangle, \langle m-4|n+5\rangle \\ &\Delta v = \pm 1, \pm 3, \pm 5, \pm 7, \pm 9 \end{aligned}$$

to the following
rules: