

## CHMY 374: Experiment #4

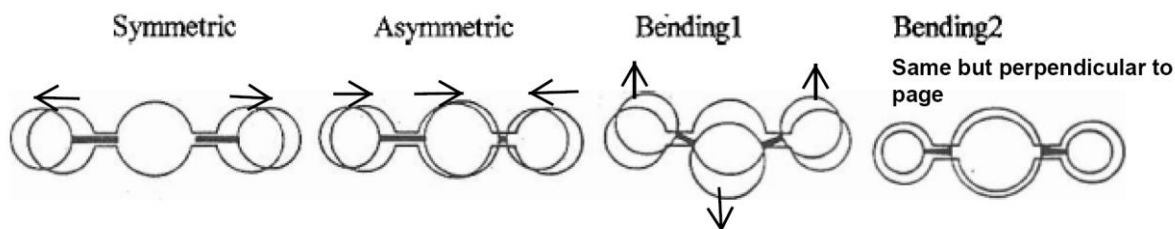
### Vibrational Spectroscopy of Polyatomic Molecules

#### Introduction

#### PART 1. N<sub>2</sub>O

The vibrational motion of molecules gives rise to *quantum vibrational zero point energy and discrete quantum energy levels* because the nuclear positions are constrained to be close to positions that minimize the electronic energy. Spectroscopy seeks to collect information about vibrational motion by observing transitions between energy levels. Such spectroscopic information is used to determine molecular structure, to explain physical properties of materials, to assist in chemical analyses, and even to study chemical reactions.

Classical mechanics is also quite useful for analyzing vibrational and rotational motion of molecular systems. (Quantum postulates are applied to understand transitions between energy levels.) Because of the spring-like nature of molecular bonds, it is possible to make several generalities about molecular vibrations. Specifically, any vibrational motion can be described by a set of normal mode vibrations. A normal mode is a very simple vibration in which all the particles in the system (or nuclei in the molecule) are moving in simple harmonic motion with exactly the same frequency. The number of independent vibrations having these characteristics is the number of vibrational degrees of freedom, which is  $3N-6$  ( $3N-5$  for a linear molecule) for a molecule with  $N$  nuclei. For example, N<sub>2</sub>O is a linear triatomic molecule and has four normal modes of vibration (and only two of rotation).



Associated with each normal mode is a vibrational frequency and a normal coordinate. The vibrational frequency is easily calculated from nuclear masses, force constants, and molecular structure parameters; or, knowing the structure and the vibrational frequencies, force constants can be calculated. The normal coordinate associated with a normal mode can be thought of as a multi-dimensional unit vector which shows in what directions the nuclei are moving relative to one another in the normal mode of vibration. Normal coordinates are important because they make it possible to describe any molecular vibration as a linear combination, or weighted vector sum of the normal modes.

Applying quantum postulates to molecular vibrations, one finds that the frequency of absorbed light is about equal to the vibrational frequency. As always, to find the rate of transition between two vibrational states of a particular normal mode,  $Q$ , one must evaluate the square of the Hamiltonian (the energy operator) matrix element connecting

the two states. As for electronic transitions, the absorption of infrared light to change vibrational state is dominated by the electric field interaction with the charges of the molecule, i.e., the dipole moment. The observed transition rates between vibrational states of a particular normal mode,  $Q$ , is therefore proportional to:

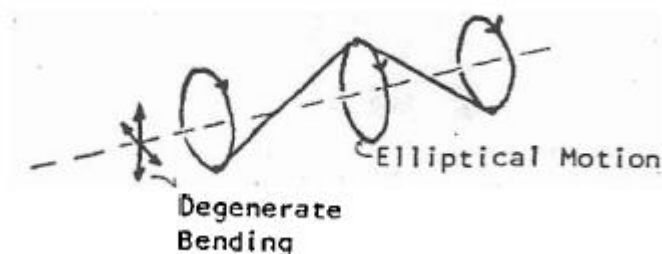
$$P_{n-m} = \left| \int \Psi_n^* \mu(Q) \Psi_m dQ \right|^2 \quad [1],$$

where  $\mu(Q)$  is the expectation value of the dipole moment in the ground electronic state, (and may or may not be a function of the nuclear positions);  $n$  and  $m$  indicate two different *vibrational states of normal mode Q*. Note that if  $\mu(Q)$  is a constant, then the integral vanishes because the wavefunctions of different energy eigenstates are orthogonal, and the transition is said to be “forbidden”. If this integral is nonzero, the transition involving excitation of that mode is said to be “allowed”. Mathematically, the important term for IR absorption and emission is that involving the first derivative of the dipole moment with respect to the normal coordinate, i.e., in the case of IR radiation, this integral will only be nonzero when the  $\partial\mu / \partial Q \times Q$  term is nonzero, where  $Q$  here stands for the displacement of the normal coordinate from its equilibrium position. In the harmonic oscillator approximation for the wavefunctions (a good approximation) the  $Q$  matrix element mathematically = 0 unless  $m = n \pm 1$ . This says that IR radiation will only be absorbed when there is a change in the dipole moment as the vibration oscillates, and the two states are adjacent in the energy level diagram. Note: the presence of a permanent dipole moment is not sufficient for absorption of IR radiation.

An important fact about the absorption of a photon is that: ***photons have total angular momentum =  $L(L+1) (h/2\pi)^2$ , with  $L=1$ , and angular momentum is ALWAYS CONSERVED. Therefore, if a photon disappears, the angular momentum must appear in the molecule.***

In at **diatomic** molecule, rotational energy in the molecule **must change**, and we will always see rotational states changing along with a vibrational state change in the spectrum (see below). For linear **polyatomics**, purely rotational effects are **nearly** identical with those for diatomic molecules: There will be a rotational constant,  $B$ , and a rotational quantum number,  $J$ , and quite similar selection rules as for diatomics.

But, linear molecules like those we study today that have *degenerate vibrations* (more than one vibration at the same energy by symmetry) can have what is termed **vibrational angular momentum**. The degenerate vibrations can add together (mix) to give a motion which has angular momentum, if they vibrate **out of phase**. This will occur for all linear polyatomics since they exhibit degenerate bending modes. This is shown for a linear triatomic.



The quantum number,  $l$ , is defined as the amount of angular momentum due to the vibration of the degenerate modes.

As mentioned, in a linear triatomic  $3N-5 = 4$  vibrational degrees of freedom and 4 quantum numbers are needed to describe the vibrational state of the molecule. Two quantum numbers will be associated with the two non-degenerate modes, symmetrical and asymmetrical stretching. Another quantum number will be  $l$ , because there are 2 degenerate modes. The fourth quantum number will be associated with the total excitation in the two degenerate modes since they are indistinguishable.

The state of the linear triatomic is then written as:

$$(v_1, v_2^l, v_3) \quad \text{where } v_1 = \text{q.n. of symmetric stretching motion}$$

$$v_2^l = \text{q.n. of bending modes}$$

$$v_3 = \text{q.n. of asymmetric stretch}$$

The identification of modes as being "symmetric stretch," etc., is done by calculation and determination of normal coordinates.

Using the transition probability expression given above, selection rules can be calculated for a given molecule. The transitions are divided up into these types:

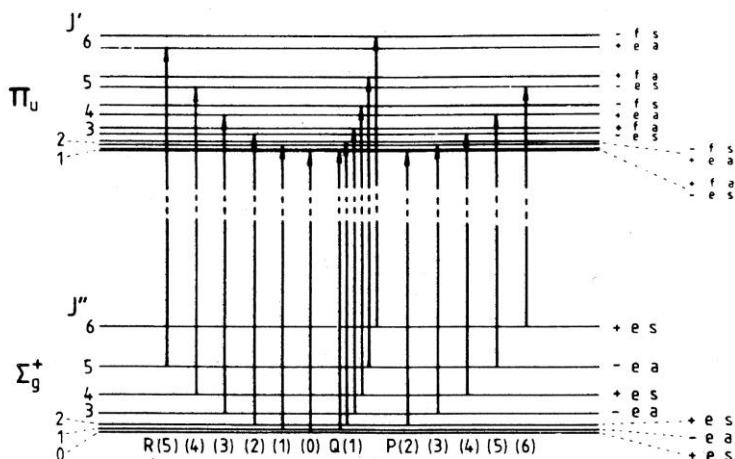
### 1) PARALLEL BANDS

When the change in dipole is parallel to the molecular axis,  $l$  cannot change (i.e.,  $\Delta l = 0$ ) since it is associated with bending only.

- a) If  $l = 0$ , then the rotational selection rule is  $\Delta J = \pm 1$  and a P and R branch are observed. A P branch is where  $\Delta J = -1$  and an R branch where  $\Delta J = +1$  (see below).
- b) If  $l \neq 0$  (only in excited states), then  $\Delta J = 0, \pm 1$  and P, Q, and R branches will be observed. Notice that since  $J$  is the total angular momentum,  $J = l, l+1 \dots$  and thus, if  $l \neq 0$ , then  $J \neq 0$ .

### 2) PERPENDICULAR BANDS

When the change in dipole is perpendicular to the molecular axis, as in the bending modes, then  $\Delta J = 0, \pm 1$  and there will be P, Q, and R branches.



**Figure 6.24** Rotational transitions accompanying a  $\Pi_u - \Sigma_g^+$  infrared vibrational transition in a  $D_{\infty h}$  linear polyatomic molecule. For  $C_{\infty v}$  the  $g$  and  $u$  subscripts and  $s$  and  $a$  labels should be dropped.

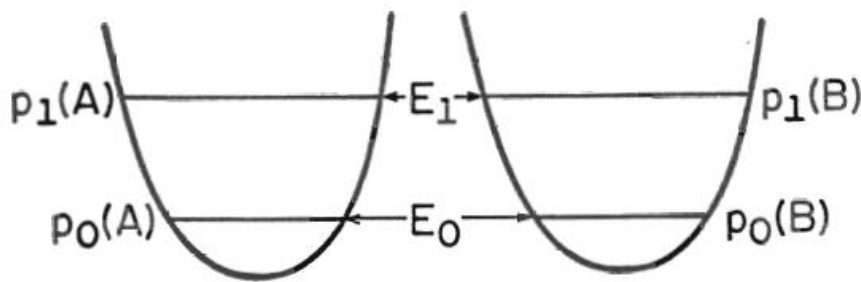
### PART 2. NH<sub>3</sub>

Ammonia and other non-planar XH<sub>3</sub> molecules have two stable equilibrium configurations and can invert between them—**at absolute zero of temperature!** This is because of *quantum mechanical tunneling*. The resulting energy level structure is more complex than that of a simple harmonic motion oscillator and, in ammonia, the energy level structure results in what has been termed "doubling" of the spectrum. The spectrum you will take will show two strong branches that are separated by about 35 cm<sup>-1</sup>. This separation is dependent on the potential barrier between the two configurations.

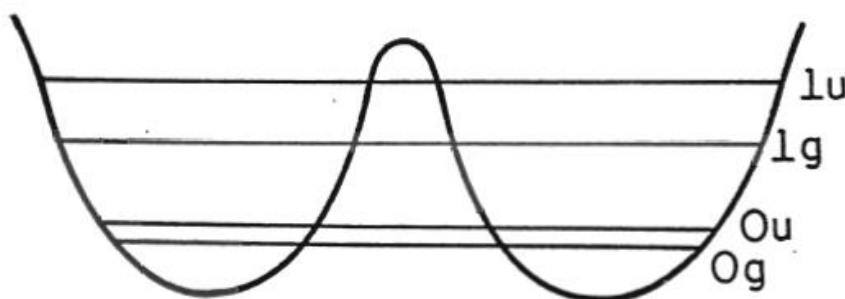
The molecular motion that leads to the absorption seen is called inversion. This is where the three hydrogen atoms on the nitrogen simultaneously switch from all being on one side of the N to all being on the other side (sometimes referred to as an umbrella-type motion).



Let's assume that ammonia cannot invert. In this case we obtain two identical isolated harmonic oscillators with an infinite barrier between them. The potential wells are too far apart for the wavefunctions to interact. Such a case is shown below.



In reality, however, the barrier to inversion in ammonia is not infinite so the above model simply provides us with a starting point for the description of the real situation. If we look at a non-infinite rise between the potential barriers, wavefunctions of equal energy can interact, either symmetrically- *gerade*, or asymmetrically- *ungerade* (g and u). g means the wavefunction does not change sign when the x, y, z are all changed to  $-x, -y, -z$  (this is general mathematical inversion—not to be confused with the umbrella inversion mentioned above). The hydrogen atoms seem to get across a high potential barrier without actually having enough energy. This effect is called tunneling, and is *ubiquitous* for low mass particles such as electrons and protons. (e.g., in the H atom 1s state, the electron is tunneling whenever it is more than 2 bohr radii away from the nucleus (which is much of the time), *a fact few people realize*).



The selection rules in IR spectroscopy inform us that only  $g \rightarrow u$  or  $u \rightarrow g$  transitions are allowed. We will be seeing the transitions from  $0g \rightarrow 1u$  and  $0u \rightarrow 1g$ . These transitions occur around  $950 \text{ cm}^{-1}$  with a separation of about  $35 \text{ cm}^{-1}$ .

## EXPERIMENTAL SECTION

Two molecules will be studied in this experiment. The first will be nitrous oxide,  $\text{N}=\text{N}=\text{O}$ , a linear triatomic. General spectrum characteristics will be observed, transitions identified as to band types, and the rotational constant, B, will be calculated from experimental data. The second molecule will be ammonia,  $\text{NH}_3$ , where the qualitative effects of inversion doubling will be observed.

Take a background infrared spectrum of the evacuated gas cell. Next, fill the cell with approximately 30 torr of  $\text{N}_2\text{O}$  gas. The gas cell has windows that will not absorb significantly in the IR range we are looking at. Take an IR spectrum from  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$ . The table below lists some intense transitions found in this range. Zoom in on these areas and plot out each range of bands (You may also do this later using a spreadsheet program). Write down the exact location of each of the peaks of interest.

cm <sup>-1</sup>	Band Type	Initial State ( $\nu_1, \nu_2', \nu_3$ )	Final State ( $\nu_1, \nu_2', \nu_3$ )
579.3	⊥	0 1 <sup>1</sup> 0	0 2 <sup>0</sup> 0
588.8	⊥	0 0 <sup>0</sup> 0	0 1 <sup>1</sup> 0
590.3	⊥	0 1 <sup>1</sup> 0	0 2 <sup>2</sup> 0
1167	∥	0 0 <sup>0</sup> 0	0 2 <sup>0</sup> 0
1285	∥	0 0 <sup>0</sup> 0	1 0 <sup>0</sup> 0
2224	∥	0 0 <sup>0</sup> 0	0 0 <sup>0</sup> 0
2462	∥	0 0 <sup>0</sup> 0	1 2 <sup>0</sup> 0
2564	∥	0 0 <sup>0</sup> 0	2 0 <sup>0</sup> 1
3481	∥	0 0 <sup>0</sup> 0	1 0 <sup>0</sup> 1

Using the same background, take an IR spectrum of the gas cell **filled** (~5-10 psi) with ammonia. The area we are interested in is around 950 cm<sup>-1</sup>. This is where the inversion doubling will be seen. Zoom in on this area of the spectrum and print out the spectrum. As above, write down the location of each of the peaks of interest.

In taking the spectra of N<sub>2</sub>O you will notice that the rotational lines are too closely spaced to be accurately resolved. In order to determine the rotational constant, assume that the intensity of each line in the P and R branches is dependent only on the population of the initial rotational state. The easiest line to use when the lines are not resolved is the maximum of each branch. The separation between corresponding lines in the two branches is equal to 4BJ, where J is the rotational level. If the peak maxima are used, the experimentally measured separation is set equal to 4BJ<sub>max</sub>, where J<sub>max</sub> is the maximally populated J level. J<sub>max</sub> is determined from the **Boltzmann distribution**, which always states that the relative population of a rotational *state*, N(J), is given by:

$$N(J) \propto g_J \exp(E(J) / k_B T) = (2J + 1) \exp(-BJ(J + 1) / k_B T) \quad [2]$$

where the degeneracy of any state with total angular momentum = J is 2J+1. (for example, a p atomic orbital has  $l = 1$  has a degeneracy = 3, the “3 p orbitals”.

By taking the derivative of N(J) with respect to J and setting this equal to zero it is found that

$$J_{\max} = \sqrt{kT/2B} - 1/2 \quad [3]$$

### Notes on Intensities and Selection Rules (January 25, 2014 P. Callis)

In the spectrum of NNO, there are two intense bands and some that are much weaker.

Why are these seen weakly instead of not being seen at all?

Three factors may influence the strength of absorption:

(a) **Angular momentum MUST be conserved.** The photon has an angular momentum of  $h/2\pi$ . The disappearance of a photon *requires* the molecule to *increase* its angular momentum by  $h/2\pi$ . This is why  $\Delta J = +$  or  $- 1$ . For linear molecules,  $J$  is actually the total angular momentum squared ( $L^2$ ) quantum number. Recall  $J^2 = J(J+1) (h/2\pi)^2$ , but there are  $2M+1$  “z components”, given by  $M h/2\pi$ , with  $M$  going from  $-J$  up to  $+J$  in steps of 1. The photon angular momentum vector may be aligned with or against that of the molecule just before absorption. The sum of the two vectors must not change when the photon is absorbed. That is why the molecule may gain or lose angular momentum upon absorption. (i.e.,  $\Delta J = +$  or  $- 1$ )

(b)  $\partial\mu / \partial q$  (the change in permanent dipole with respect to the change of the normal coordinate) must be non-zero. Sometimes this is exactly  $= 0$  by symmetry. If not zero by symmetry, it can be very small, medium, or large, depending on the nature of the vibration, and the intensity is proportional to its square.

(c) **Boltzmann factor.** Hot bands (those originating from thermally excited rotational and vibrational states) may be observed depending on the ratio of the energy of the state above the zeropoint relative to  $kT$  (which, you should recall by now, is about  $200 \text{ cm}^{-1}$  at room temperature).

## IMPORTANT POINTS

In your write up, be sure to display understanding upon completing the following points:

- 1) Measure the spacing between P and R branch maxima for all  $\text{N}_2\text{O}$  parallel bands.
- 2) Calculate the rotational constant,  $B$ , (in  $\text{cm}^{-1}$ ) for each observed transition.
- 3) Calculate the moment of inertia,  $I$ , found from  $B$  obtained in 2.
- 4) The bond length between each atom is shown below. Using this information and the mass of each atom, calculate  $I$  using:

$$I = \sum_i m_i (x_i - x_c)^2 \quad [4]$$

$$\text{where } x_c = \text{center of mass} = \frac{\sum_i m_i x_i}{\sum_i m_i}$$

and  $x$  is the position of the  $i$ th mass along the bond axis relative to whatever origin you choose.

$\text{N}_{(1)}=\text{N}_{(2)}=\text{O}_{(3)}$  Bond lengths:  $r_{1,2} = 1.26\text{\AA}$ ,  $r_{2,3} = 1.19\text{\AA}$ ,  $r_{1,3} = 2.45\text{\AA}$

- 5) Discuss why the rotational lines are too closely spaced to be accurately resolved.
- 6) Describe the four vibrational modes of  $\text{N}_2\text{O}$ . In what modes is angular momentum observed? Why?
- 7) Show the doublet separation measured at  $950\text{ cm}^{-1}$  in the vibrational spectrum of  $\text{NH}_3$ . How close is it to the literature value of  $36.5\text{ cm}^{-1}$ ?
- 8) Discuss the origin of inversion doubling in the vibrational spectrum of  $\text{NH}_3$ . Make a schematic energy level diagram (similar to the one included in this document) illustrating inversion doubling (showing the wavefunctions and the transitions) in the vibrational spectrum of the umbrella mode in  $\text{NH}_3$ . Briefly mention the meaning of the ***g*** and ***u*** designations, and whether the molecular dipole is ***g*** or ***u***, and how this dictates the selection rules involved?

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### History:

From VibrationalSpectroscopy08.doc 19feb08 Minton;  
374-11-Vibrational-II.pdf 17feb11; CHMY 374-14 Experiment #3 For January 29, 2014 (modified by P. Callis)  
For February 16, 2017 and February 15, 2018 (modified by P. Callis)

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