CHMY 374: Experiment #4  
Vibrational Spectroscopy of Polyatomic Molecules

Introduction

PART 1. N₂O

The vibrational motion of molecules gives rise to discrete energy levels. 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 used in 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
Fig. 10.41  Energy-level diagram for infrared absorption, elastic (Rayleigh) scattering, and inelastic (Raman) scattering. Transitions between vibrational energy levels of the ground electronic state absorb infrared radiation; not all transitions are allowed. For elastic scattering the frequency of the incident light is equal to the frequency of the scattered light. For inelastic scattering the frequency of the scattered light is different from that of the incident light. The virtual state shown can have any energy; the scattering of light occurs in any region of the spectrum.
A glowing hot bar of metal

Mirror moves back and forth causing each wavelength to interfere at different times
Interferogram

IR light intensity from ALL FREQUENCIES AT ONCE interfering with each other at a particular time
The Fourier Transform of the interferogram provides the spectrum of the light.

Fourier Transform is the technical term for nothing more than:

All the overlap integrals of $\cos(2\pi vt)$ with the interferogram.

The amplitude of the overlap integral for a particular frequency = intensity of light at that frequency
The Interferometer
FIG. 3. Simplified diagram of an Advanced LIGO detector (not to scale). A gravitational wave propagating orthogonally to the detector plane and linearly polarized parallel to the 4-km optical cavities will have the effect of lengthening one 4-km arm and shortening the other during one half-cycle of the wave; these length changes are reversed during the other half-cycle. The output photodetector records these differential cavity length variations. While a detector's directional response is maximal for this case, it is still significant for most other angles of incidence or polarizations (gravitational waves propagate freely through the Earth). Inset (a): Location and orientation of the LIGO detectors at Hanford, WA (H1) and Livingston, LA (L1). Inset (b): The instrument noise for each detector near the time of the signal detection; this is an amplitude spectral density, expressed in terms of equivalent gravitational-wave strain amplitude. The sensitivity is limited by photon shot noise at frequencies above 150 Hz, and by a superposition of other noise sources at lower frequencies [47]. Narrow-band features include calibration lines (33–38, 330, and 1080 Hz), vibrational modes of suspension fibers (500 Hz and harmonics), and 60 Hz electric power grid harmonics.
Transmittance Spectrum of air only from our IR spectrophotometer

- CO$_2$ Bending
- H$_2$O Bending
- CO$_2$
- H$_2$O Stretching

Air only (transmittance)
Background
This is what is subtracted
Absorbance Spectrum of air only from our IR spectrophotometer

- **Air only**
- **Background**
- **This is what is subtracted**

**Wavenumbers**

- **CO₂ Bending**
- **H₂O Bending**
- **CO₂**
- **H₂O Stretching**
The 3N-5 = 4 normal modes for the linear molecules NNO and CO2
Ab initio computation of vibrational modes and frequencies

$\text{CO}_2 \text{ vs. N}_2\text{O}$

$\text{OCO} \text{ vs. NNO}$
Both have 22 electrons

atomic number of C = 6
atomic number of N = 7
atomic number of O = 8

Start with OCO
Take a proton out of left O and give to C
= NNO
Degenerate Bending Elliptical Motion
NNO low pressure
NNO higher pressure
NNO higher pressure
Q branch: $\Delta J=0$ for rotational motion

Why is this so intense and sharp???
Notes on Intensities and Selection Rules

In the spectrum of NNO, there are two intense bands and some that are much weaker. Why are these weak instead of not being seen at all.

Three factors may influence the strength of absorption:

(a) Angular momentum must be conserved!

The PHOTON has angular momentum \( = 1 \hbar/2\pi \)

So, the molecule must increase or decrease by the same amount.

Components \( M \) given by \( M \hbar/2\pi \), with \( M \) going from \(-J\) up to \(+J\) in steps of 1. The photon angular momentum vector may by 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 and $kT$.

d) break down of $\Delta n = +$ or $-1$ for harmonic oscillator (recall HCl)
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.
   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, $J = l, l+1 \ldots$ 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.
For a linear molecule like $\text{N}_2\text{O}$, $\Delta J$ rotational can be $+1$ or $-1$ because the angular momentum change can be in the degenerate BENDING VIBRATIONS. For $\Delta J = 0, \pm 1$, $J' = J''$ results in so many transitions with almost the same $\Delta E$. 

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.
Assignments for N$_2$O

These questions are about the bands of N$_2$O. You may use a spreadsheet program to help with this. Write down the exact location of each of the peaks of interest.

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>Band Type</th>
<th>Initial State $(v_1, v_2^l, v_3)$</th>
<th>Final State $(v_1, v_2^l, v_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>579.3</td>
<td>$\perp$</td>
<td>0 $1^1 0$</td>
<td>0 $2^0 0$</td>
</tr>
<tr>
<td>588.8</td>
<td>$\perp$</td>
<td>0 $0^0 0$</td>
<td>0 $1^1 0$</td>
</tr>
<tr>
<td>590.3</td>
<td>$\perp$</td>
<td>0 $1^1 0$</td>
<td>0 $2^2 0$</td>
</tr>
</tbody>
</table>

**Example**

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>Band Type</th>
<th>Initial State $(v_1, v_2^l, v_3)$</th>
<th>Final State $(v_1, v_2^l, v_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1167</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>0 $2^0 0$</td>
</tr>
<tr>
<td>1285</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>1 $0^0 0$</td>
</tr>
<tr>
<td>2224</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>0 $0^0 1$</td>
</tr>
<tr>
<td>2462</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>1 $2^0 0$</td>
</tr>
<tr>
<td>2564</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>2 $0^0 0$</td>
</tr>
<tr>
<td>3481</td>
<td>$\parallel$</td>
<td>0 $0^0 0$</td>
<td>1 $0^0 1$</td>
</tr>
</tbody>
</table>

Using the same background, take an IR spectrum of the gas cell filled with ammonia. The area we are interested in is around 950 cm$^{-1}$. This is where the inversion doubling will be...
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. The hydrogen atoms seem to get across a high potential barrier without actually having enough energy. This effect is called tunneling.

The selection rules in IR spectroscopy inform us that only g→u or u→g transitions are allowed. We will be seeing the transitions from 0g→1u and 0u→1g. These transitions occur around 950 cm⁻¹ with a separation of about 35 cm⁻¹.
Two non-interacting vibrating systems (harmonic oscillators)
Tunelling

Left-hand energy well (a)  Right-hand energy well (b)

$\uparrow$ Microwave  $25 \times 10^9$ Hz

$\downarrow$ Microwave  $25 \times 10^9$ Hz

Senior Sophister 2011

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