Experiment 11

IR SPECTRUM AND NORMAL VIBRATIONS OF CARBON DIOXIDE

**Degrees of Freedom**

Whereas a previous laboratory experiment involving the IR absorption spectra of HCl and DC1, the present experiment deals with a linear, triatomic molecule. From the statistical mechanical treatment of gaseous molecular heat capacities it is necessary to consider the concept of degrees of freedom. For a linear triatomic,

- there are 3 spatial coordinates (X, Y, Z)
- there are 3 atoms per molecule
- \(3 \times 3 = 9\) degrees of freedom per molecule
- \(3\) = translational degrees of freedom
- \(2\) = rotational degrees of freedom
- \(9-(3+2) = 4\) degrees of freedom remain

Thus, a linear, triatomic molecule has four characteristic vibrations. (Note that the rotation about the central axis of a linear molecule does not make a statistical contribution.)

In order for a characteristic vibration to be infrared active, there must be a change in the dipole moment of the molecule as it executes the vibrational motion. Each IR-active vibration will appear as a band of lines due to simultaneous changes in the rotational energy. (In the case of HC1, the rotational structure of the band was resolvable using the FTIR spectrometer in the laboratory. However, for many molecules the rotational structure will not be resolvable with this instrument.)

**Normal Vibrations**

Now, let us look more closely at what is meant by characteristic vibrations. Consider a triatomic molecule of arbitrary shape. Let the bonds be represented by springs, with a third spring added to represent resistance to bending (i.e. changing the bond angle).
If one of the atoms is tapped in an arbitrary direction, the whole molecule will be set into vibration. In general, this vibratory motion will be very complicated and will vary with time. However, if the springs follow Hooke's law, which will be the case for small amplitude vibrations, the motion will always be the superposition of simple harmonic motions. In the case of our linear triatomic, four such harmonic motions are required. These are the characteristic vibrations referred to above and are called the normal vibrations.

Suppose the molecule is actually executing one of the normal vibrations, rather than a complicated superposition of all possible normal modes. Then, each atom will be executing a back-and-forth motion in a direction characteristic of that mode and at the same frequency as the others. Suppose the motion is along the X-axis for atom 1. Since the motion is sinusoidal (harmonic), application of Newton's law of motion will lead to the following equation for the restoring force acting on atom 1.

\[ X_1 = \text{displacement of atom 1 from equilibrium position} \]
\[ F_1 = \text{restoring force} = (m_1) \left( \frac{d^2X_1}{dt^2} \right) \]
\[ X_1 = \sin (2\pi\nu t) = \sin \omega t \]
\[ \omega = 2\pi\nu = "\text{circular frequency}" \]
\[ \frac{d^2X_1}{dt^2} = -\omega^2 \sin \omega t = -\omega^2 X_1 \]
\[ F_1 = -(m_1)\omega^2 X_1 \]

There is a series of such restoring-force equations for all the atoms and all three directions in space. If each F is related to the bond force constants (k’s) of the molecule (i.e. the force constants of the appropriate springs), the roots of this set of simultaneous equations will be the normal frequencies as functions of the k’s and the atomic masses. To the degree that the k’s represent the molecule accurately, the calculated normal frequencies will agree with the observed values.

This method can be demonstrated with the relatively trivial case of a diatomic molecule, for which vibratory motion can only be along the molecular axis.

First, let atom 2 be fixed \((X_2 = 0)\) and move atom 1. Then move atom 2 with atom 1 fixed. Finally, add the two effects.

\[ F_1 = -kX_1 \ (X_2 = 0) \]
\[ F_1 = kX_2 \ (X_1 = 0) \]
Total $F_1 = k(X_2 - X_1) = -m\omega^2 X_1$

Similarly, for the restoring force on atom 2, we get

$F_2 = k(X_1 - X_2) = -M\omega^2 X_2$

These rearrange to

$(k-m\omega^2)X_1 - kX_2 = 0$

$-kX_1 + (k-M\omega^2 X_2 = 0$

The solutions are given by solving the determinental equation

$$\begin{vmatrix} (k - m\omega^2) & -k \\ -k & (k - M\omega^2) \end{vmatrix} = 0$$

whose roots are

$\omega = 0$, only translation, no vibration

$\omega = \left[\frac{k(m+M)}{mM}\right]^{1/2} = 2\pi\nu$

Notice how the reduced mass has appeared in a natural way.

Now, consider the quantum mechanical version (as given in the HC1 experiment handout, for example).

$$h\nu (\nu = 0 \rightarrow \nu = 1) = \left(\frac{h}{2\pi}\right)\left[\frac{k(m+M)}{mM}\right]^{1/2}$$

Hence, our "classical" result must be multiplied by Planck's constant to get the right energy.

**Normal Coordinates**

In order to decide which vibrations (\(\omega\)'s) are IR-active, we need a picture of the vibratory motion associated with each frequency. Again, the trivial diatomic case will serve as an example. First, we substitute our answer for \(\omega\) into the two simultaneous equations. The calculation goes as follows.

\[k - m\omega^2 = -k(m/M), \quad k - M\omega^2 = -k(M/m)\]

Let \(X_1 = +1\) (atom 1 moving to the right)
\[-k(m/M)(+l) - k X^2 = 0\]
\[-k(+l) - k(M/m) X^2 = 0\]

\[X_2 = -m/M\]

A picture of the normal vibration is given below.

Experimental. I. Normal Coordinate Analysis

The carbon dioxide molecule can be thought of as containing two polar bonds.

The normal modes of vibration are as follows.

1. Is CO₂ polar or nonpolar? In which of the normal modes does the polarity of the molecule change during one back-and-forth motion? Label these "IR-active".
2. There are four vibrational degrees of freedom. The fourth mode is one of the above, but in a different direction. Only one of the modes can move in two independent directions. Which one is it?

3. Perform a normal coordinate analysis of the axial (stretching) modes, 1 and 3, only. This keeps the analysis down to one dimension. To begin refer to the simple picture:

\[ F_1 = k(X_2 - X_1) = -m\omega^2 X_1 \]

and the equation:

The analysis should result in (a) two frequencies in terms of the force constant and the masses, and (b) a diagram of the modes of motion for each frequency.

**Experimental. II. IR Spectrum**

1. Fill an IR gas cell with one atmosphere of CO\(_2\). Either use the portable vacuum line and a "lecture bottle" or flush the cell with CO\(_2\) from one of the larger tanks.

2. Scan the whole range. Identify the strong peaks; these are the normal modes.

3. With the aid of the vacuum system, reduce the pressure of CO\(_2\) in the cell until the resolution of the peaks is maximized.

4. The [perpendicular] bending mode has a central peak, called the Q-branch. The [parallel] stretching modes have only P and R branches. Assign the major peaks, i.e., \(v_2\) and \(v_3\).

5. Using your normal coordinate analysis, estimate the frequency of the missing mode (the IR-inactive one).

6. "Combination bands" and "overtones" sometimes appear, although weaker than single normal modes. Look at the 1 atmosphere scan. Can any of the following be identified?

\[ v_1 + v_2, \ v_1 + v_3, \ 2v_2 + v_3, \ 3v_2, \ 2v_1 + v_3 \]

With the available information can the frequency of the IR-inactive mode be assigned?
7. Measure the IR spectrum of another linear molecule, CS$_2$. Pump out any remaining CO$_2$ and vent to the atmosphere. In a hood add no more than two drops of CS$_2$ with a dropping pipette. Measure the IR spectrum. If some peaks are overscale, reduce the concentration in the cell with the vacuum system. At the end of the experiment pump out the cell.

8. Construct a CO$_2$ data file for the normal coordinate program and find values of the force constants that lead to vibrations agreeing with the analysis of the experimental data. List these force constants and calculated energies for $\nu_1$, $\nu_2$, and $\nu_3$. The bond length in CO$_2$ is 1.16 Å. Repeat the analysis for CS$_2$ whose bond length is 1.58 Å.

**Illustrative Problem**

Carbon monoxide vibrates at 2143 cm$^{-1}$ and the CO bond has a bond order of 3 (triple bond). Estimate the vibrational frequency of NO, which has a bond order of 2.5. Assume that the bond force constant is proportional to the bond order.

Answer: 1875 cm$^{-1}$