Microwave Spectroscopy

Introduction

In this experiment, rotational spectra are collected using a microwave spectrometer. Initially, the structure of a linear molecule OCS is determined by measuring the frequency of the zero-field $J = 2 \leftarrow 1$ transition for isotopically-substituted OCS molecules. In the second part of the experiment, the the dipole moment of NH_3 is determined from the frequencies of the (3,3) NH_3 inversion when different Stark voltages are applied to the sample cell. The latter calculation requires a knowledge of the cell spacing. The cell is calibrated with OCS, a molecule for which the dipole moment is very precisely known.

Theory

In the absence of electric and magnetic fields, the rotational energies of a non-linear polyatomic molecule depend, to high accuracy, on only three molecular constants called the rotational constants. These constants are usually called A_v, B_v, and C_v, where the subscript v indicates a dependence on the vibrational state of the molecule. In the ground vibrational state, all vibrational quantum numbers are zero, and it is conventional to write:

$$A_0 = \frac{h}{8\pi^2 I_0^a} \qquad B_0 = \frac{h}{8\pi^2 I_0^b} \qquad C_0 = \frac{h}{8\pi^2 I_0^c}$$

where, I_0^a, I_0^b, and I_0^c are the "effective" moments of inertia of the molecule about the *a*-, *b*-, and *c*-principal inertial axes, respectively. Ordinarily, the rotational constants are labeled such that $A_0 \geq B_0 \geq C_0$.

The moment of inertia I_0^a is:

$$I_o^{(a)} = \sum_{k=1}^{N} M_k \left(b_k^2 + c_k^2 \right)$$

where b_i and c_i are the coordinates of the atom i whose mass is M_i. If the structure of the molecule is known, the coordinates b_i and c_i can be calculated for the N atoms by trigonometry from the bond distances and bond angles. Conversely, it is often possible to use the expression for I_o^a together with similar equations for I_o^b and I_o^c, to determine the bond distances and bond angles from experimentally determined values of A_0, B_0, and C_0.

Molecules are classified based upon the moments of inertia about the three axes as shown in Table I. By our convention, the *a*-axis in the symmetric top molecules is the rotational axis about which the rotation has the smallest moment of inertia. The rotational energies of molecules are quantized and labeled with the quantum number J.

Table I: Rotational Classification of Molecules

Type		Molecular Example	Macroscopic Example
Linear	$I_o^a \neq I_o^b$	CO_2, OCS	Round pencil
Spherical top	$I_o^a = I_o^b = I_o^c$	CH_4	Ball
Symmetric top (prolate)	$I_o^a \neq I_o^b = I_o^c$	CH_3Cl	Square pencil
Symmetric top (oblate)	$I_o^a = I_o^b \neq I_o^c$	Benzene	Penny
Asymmetric top	$I_o^a \neq I_o^b \neq I_o^c$	Water	

The total rotational angular momentum of a molecule is determined by a quantum number J, as follows:

$$\hat{J}^2 \, \psi_{j,k,m} = J(J+1) \; ^2 \, \psi_{j,k,m} \, .$$

Here, $\psi_{j,k,m}$ is an eigenfunction of the total rotational energy operator in addition to being an eigenfunction of the square of the rotational angular momentum. The quantum number J must be zero or positive integer:

$$J = 0, 1, 2, 3, \ldots .$$

For a symmetric top, either prolate or oblate, the quantum number K determines the vector component of the angular momentum about the molecular symmetry axis, which is the a-axis for a prolate top or the c-axis for an oblate top. Thus, if we call this axis the z-axis,

$$\hat{J}_z \, \psi_{j,k,m} = K \;\; \psi_{j,k,m}$$

The quantum number K must be an integer between $+J$ and $-J$, so that K is one of the numbers,

$$K = 0, \pm 1, \pm 2, \ldots, \pm J \; .$$

The energy of a symmetric top molecule depends on K because rotation about the symmetry axis and tumbling end over end are very different motions, so the relative amounts of angular momentum about the different axes strongly affect the energy. The sign of K signifies the direction of the rotation about the z-axis. Energies are degenerate for $+K$ and $-K$, since a simple change of direction does not change the total energy.

The quantum number m determines the component of the total rotational angular momentum about a space-fixed (laboratory) Z-axis. Thus,

$$\hat{J}_Z \, \psi_{j,k,m} = m \;\; \psi_{j,k,m} \, .$$

In the absence of electric or magnetic fields, the rotational energy of a molecule does not depend on the quantum number m. This is a result of the fact that space is isotropic, so that the energy of a molecule cannot depend on the orientation of its rotational motion in space. The quantum number m also must be an integer between $+J$ and $- J$, so:

$$m = 0, \pm 1, \pm 2, \ldots, \pm J \; .$$

Since there are apparently *2J+1* values of *m* for each *J, K* combination, the rotational energy levels of a symmetric top molecule have a degeneracy of *2(2J+1)* for $K \neq 0$ ($-K$ and $+K$ are degenerate) and *2J + 1* for $K = 0$.

The selection rules for absorption or emission of radiation by a symmetric top molecule are:

$$\begin{aligned} \Delta J &= 0, \pm 1 \\ \Delta K &= 0 \\ \Delta m &= 0 \end{aligned}$$

Normally, for absorption of a photon, $\Delta J = +1$ and $\Delta K = 0$ since $E_{J'K} > E_{JK}$ if $J' > J$. An exception is the ammonia molecule to be discussed below.

The eigenvalues of the rotational energy for a symmetric top molecule are, to good approximation:

$$E_{J,K} = hB_o J(J+1) \quad + \quad h(A_o - B_o)K^2 \quad (prolate)$$
$$E_{J,K} = hB_o J(J+1) \quad + \quad h(C_o - B_o)K^2 \quad (oblate)$$

Application of the selection rules leads to absorption frequencies of:

$$\nu\,(J+1, K \leftarrow J, K) = 2B_o\,(J+1)$$

for either prolate or oblate molecules.

Much of the foregoing is applicable to linear molecules by simply setting $K = 0$. This is because there is no rotational angular momenta of the nuclei about the axis of a linear molecule. Thus, $\langle J_z \rangle = 0$. Therefore, the energy eigenstates of a linear molecule are determined by only two quantum numbers *J* and *m* and the degeneracy of the *m* states for a given *J* is *2J + 1*. The rotational energy of a linear polyatomic molecule is:

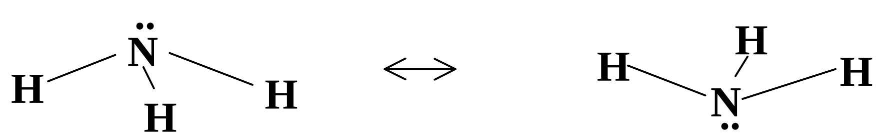
$$E_J = hB_o\, J\,(J+1) \quad \text{since } K = 0.$$

Application of the selection rules for absorption, $\Delta J = +1$ and $\Delta m = 0$, leads to

$$\nu\,(J+1 \leftarrow J) = 2B_o\,(J+1),$$

which will be recognized as the same formula as that for a symmetric top molecule. It should be mentioned, however, that the effects of a phenomenon called "centrifugal distortion" alters the energies and frequencies slightly so that symmetric top spectra usually show perceptible splitting for the different values of *K*, whereas this splitting is absent for a linear molecule (since $K = 0$ only).

The ammonia molecule is an exception to the above discussion since the famous "inversion" or "umbrella" motion of this molecule:



destroys the ± *K* degeneracy and leads to an inversion splitting that depends slightly on *J* and *K*. In a symmetric top without inversion, each *J, K* level consists of two states ($+K$ and $-K$). Each of these has an additional *2J + 1* degeneracy due to the *2J+1* possible values of *m*. In ammonia, these levels split into two groups of $2J+1$ levels. In the ground vibrational state this "inversion splitting" is ~ 0.7 cm^{-1}, whereas the typical rotational energy separations are ~ 20 cm^{-1} (B ~ 10 cm^{-1}). Transitions between states of the same J, K, and m in adjacent inversion states are strongly allowed and lead to intense microwave spectra. These transitions are labeled by their J and K values (the frequencies do not depend on m in zero field). Thus, the very intense (3,3) transition near 23,870 MHz is a transition between the J = 3, K = 3 rotational level in the ground vibrational state and the J = 3, K = 3 rotational level in the first excited inversion level. It is this transition energy that will be studied in Part 2 of this experiment.

Stark Effect

The effect of an applied electric field on a polar gas sample at low pressure is to shift the rotational energies, a phenomenon known as the "rotational Stark effect." The origin of this shift in energy is a result of the orienting effect of the attraction of the positively charged plate for the negative end of the polar molecule and of the negatively charged plate for the positive end of the molecule. These attractions (and the corresponding repulsions) interfere with the rotational motion of the molecule and thereby shift the rotational energies. The shift in the rotational energy created by an electric field depends on the orientation of the rotational motion of the molecule with respect to the direction of the applied field. The field is normally assumed to be in the $+Z$ space-fixed direction, and we already know that the projection of the angular momentum of the molecule in the $+Z$ space-fixed direction is $m\hbar$. Thus, the shift in rotational energy, as a result of the Stark effect, depends on the m quantum number as well as on J and K.

The Stark shift is most commonly computed by perturbation theory and found to be given as a power series in the applied field. Thus, if

$$E = E^{(R)} + E^{(S)}$$

where $E^{(R)}$ is the rotational energy in the absence of a field and $E^{(S)}$ is the Stark shift,

$$E^{(S)} = E^{(1)}\,\varepsilon + E^{(2)}\,\varepsilon^2 + \ldots$$

in which ε is the applied electric field. For polar symmetric tops without inversion, the levels with $k \neq 0$ show a "first-order Stark effect," which means that $E^{(1)} \neq 0$. For virtually all other molecules, $E^{(1)} = 0$ for all levels. When $E^{(1)} = 0$, the second-order term ($E^{(2)}\varepsilon^2$) dominates, but is usually much smaller than a typical first-order term. Thus, most molecules are said to have a "second-order" rotational Stark effect.

For linear molecules or symmetric tops with inversion, it is possible to write

$$E^{(2)}_{JKm} = \left(A_{JK} + B_{JK}m^2\right)\mu_o^2$$

where A_{JK} and B_{JK} are constants for a given J,K that depend on the structure of the molecule, and μ_O is the permanent electric dipole moment of the molecule. Thus, the full rotational energy for the state ψ_{JKm} is $E_{JKm} = E^{(R)}_{Jkm} + h\left(A_{Jk} + B_{Jk}m^2\right)\mu_o^2\varepsilon^2$. (It is important not to confuse the A_{JK} and B_{JK} here with the A_0 and B_0 rotational constants introduced earlier. This potential confusion should have been avoided when the theory of the Stark effect was first worked out, but it is now too entrenched to change.) The frequency of a transition is given by the Bohr frequency condition as

$$\mathrm{h}\nu(J'K'm' \leftarrow J''K''m'') = \left[E^{(R)}_{J'k'm'} + h\left(A_{J'k'} + B_{J'k'}m^2\right)\mu_o^2\varepsilon^2\right] - \left[E^{(R)}_{J''k''m''} + h\left(A_{J''k''} + B_{J''k''}m^2\right)\mu_o^2\varepsilon^2\right]$$

or

$$\nu(J'K'm' \leftarrow J''K''m'') = \nu_o(J'K'm' \leftarrow J''K''m'') + (\Delta A + \Delta B m^2)\,\mu_0^2\varepsilon^2$$

where: $$h\nu_0 = E^{(R)}_{J'K'm'} - E^{(R)}_{J''K''m''} ,$$

$$\Delta A = A_{J'K'} - A_{J''K''} ,$$

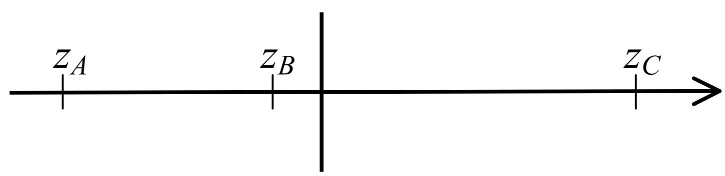
and $$\Delta B = B_{J'K'} - B_{J''K''} .$$

If the zero field spectrum is known, it is possible to calculate ΔA and ΔB to high accuracy. Since this is a linear equation, the dipole moment μ_0 can be determined from the slope of a plot of rotational frequency ν versus the square of the applied field, ε^2.

Molecular Structure

It is often possible to determine the bond distances and bond angles in a molecule from the measured rotational frequencies because the rotational constants depend upon the moments of inertia of a molecule, which in turn depend upon the molecular structure. As a simple example, we consider a linear triatomic molecule **ABC** with internuclear distances r_{AB} and r_{BC}, as follows:

The masses of the three atoms are M_A, M_B, and M_C. To calculate the moment of inertia, we assume that the z-axis is coincident with the internuclear line and that the origin of the coordinate system is at the center-of-mass of the molecule. For example,



Then, the center of mass condition is

$$M_A z_A + M_B z_B + M_C z_C = 0 ,$$

and the moment of inertia is

$$I = M_A z_A^2 + M_B z_B^2 + M_C z_C^2 \cdot$$

Finally, the bond lengths $r_{AB} = z_B - z_A$ and $r_{BC} = z_C - z_B$.

From the discussion above, it was seen that the moment of inertia I could be determined from the rotational spectrum. This, together with the center-of-mass condition is insufficient for determination of the three coordinates z_A, z_B, and z_C. It is therefore necessary to obtain additional information to determine the bond lengths. One way to obtain additional information about the structure is to measure the rotational spectrum for a sample in which one of the atoms is an isotopic variant of the most common naturally occurring species. For example, suppose the **C** atom was substituted giving a molecule with masses M_A, M_B, and $M_C{}' \neq M_C$. In the fixed nucleus approximation for electronic structure, this change does not change the structure of the molecule since the structure depends only on the nuclear charges and the number of electrons, neither of which is changed by isotopic substitution. We will therefore assume that r_{AB} and r_{BC} are the same in **ABC** and **ABC′**. Actually, because the masses affect the vibrational motion and vibrational energies and because r_{AB} and r_{BC} are vibrational averages of the bond lengths, the effective distances in the two species are slightly different. Nevertheless, it turns out that by making this assumption we can obtain a very good estimate of the structure.

The goal of the following derivation it to develop an equation which relates the difference between the moment of inertia of **ABC** (I) and that of **ABC'** (I') to the position of the isotopically-substituted atom z_C. Assume that **ABC** has a mass of M and that **ABC'** has a mass of M'.

To see how to proceed, it is easiest to use a formal treatment. To do this we write:

$$\Sigma M_i z_i = 0 \qquad \text{(i = } A,B,C \text{ for molecule } \mathbf{ABC}) \tag{1}$$

and

$$I = \Sigma M_i z_i^2 \; . \tag{2}$$

When one of the masses is changed, the center of mass moves. We let z_o be the center of mass of the isotopically-substituted molecule (**ABC'**) in a coordinate system centered at the center of mass of the original or "parent" molecule (**ABC**). Then, the center-of-mass condition is

$$\Sigma M_i' z_i = M' z_o \tag{3}$$

and

$$I' = \Sigma M_i' (z_i - z_o)^2 \; . \tag{4}$$

Only one of the M_i' is different from the corresponding M_i. If this atom is the **C** atom, we let

$$M_c' = M_c + \Delta M_c \tag{5}$$

and $M_i' = M_i$ for all i except **C**. Then,

$$\Sigma M_i' z_i = \Sigma M_i z_i + \Delta M_c z_c \; . \tag{6}$$

Since $\Sigma M_i z_i = 0$ (because the origin is the center of mass of the parent) and $\Sigma M_i' z_i = M' z_o$ (Eqn (3)) this equation becomes:

$$M' z_o = \Delta M_c z_c \tag{7}$$

which upon rearrangement gives:

$$z_o = \Delta M_c z_c / M' \; . \tag{8}$$

We now have a convenient relationship between the position of the new center of gravity z_0 and the change in mass of **C** (ΔM_C), the position **C** (z_C), and the mass of **ABC'** (M'). This will be used later on in the derivation.

Expansion of Eqn. (4) gives:

$$I' = \Sigma M_i' z_i^2 - 2 z_o \Sigma M_i' z_i + z_o^2 \Sigma M_i' \; . \tag{9}$$

By substituting $\Sigma M_i' z_i = M' z_O$ and $\Sigma M_i = M'$ into the second and third terms on the right, respectively, and combining them, the equation can be reduced to:

$$I' = \Sigma M_i' z_i^2 - M' z_o^2 \; . \tag{10}$$

As in Eqn. (6), the first term on the right can be written in terms of the parent mass and the change in mass that occurred when **C'** was substituted for **C**:

$$\Sigma M_i' z_i^2 = \Sigma M_i z_i^2 + \Delta M_c z_c^2$$
$$= I + \Delta M_c z_c^2 \quad . \tag{11}$$

Substitution of Eqn (11) into Eqn (10) gives:

$$I' = I + \Delta M_c z_c^2 - M' z_o^2 \ , \tag{12}$$

and using the relationship for z_0 in Eqn (8) leads to:

$$I' = I + \Delta M_C z_C^2 - M' \left(\frac{\Delta M_C z_C}{M'} \right)^2 \tag{13}$$

This can be written as:

$$I' - I = \mu z_c^2 \tag{14}$$

in which:

$$\mu = \Delta M_C - \frac{\Delta M_C^2}{M'} = \frac{(M' - \Delta M_C)\Delta M_C}{M'}$$

or:

$$\mu = \frac{M(M' - M)}{M'} \tag{15}$$

The net result of all of this is that measurement of the rotational spectrum of a parent species and a singly-substituted isotopic species allows calculation of I and I', from which z_c, the z-coordinate of the substituted atom may be calculated. If this process is repeated for each of the atoms, all of the coordinates may be determined, and from the coordinates, the bond distances may be calculated.

In the process just described, it is possible in principle to determine all of the coordinates for a linear triatomic molecule after measuring the spectra for just one isotopically-substituted molecule. In our **ABC** example above, we had 3 coordinates to determine and only 2 pieces of information (the moment of inertia and the center-of-mass condition). Therefore, one additional piece of information should be sufficient. This analysis is in fact correct; only one isotopic substitution is necessary. However, the vibrational averaging problem described above leads to errors in the bond distances that are larger when only one isotopic substitution is performed than when the individual coordinates are obtained by the procedures just described. The structure obtained by single isotopic substitution of each of the atoms in the molecule is called the "substitution structure" or "r_S structure", and considerable theoretical and experimental evidence has shown that it is worth the extra effort to obtain this structure when possible.

Part. 1 The Structure of the OCS Molecule

In the accompanying theoretical discussion, it is shown that for a linear molecule,

$$I' - I = \mu z_C^2$$

where I is the moment of inertia of a specific isotopic species of the molecule which we will call the "parent" species; I' is the moment of inertia of a species that differs from the parent by having one atom **C** isotopically substituted; z_C is the the z-axis coordinate of the substituted atom in a coordinate system whose origin is at the center of mass of the parent molecule and whose z-axis is the molecular axis; and

$$\mu = \frac{M(M'-M)}{M'}$$

where M and M' are the molecular masses of the parent and substituted molecules, respectively. The moments of inertia of the molecules are related to the B_0 rotational constants, as follows:

$$I = \frac{h}{8\pi^2 B_0}$$

where h is Planck's constant. The moment of inertia can be conveniently calculated in units of u·Å^2 using the following equation:

$$I = \frac{505{,}379}{B_0}$$

where B_0 is expressed in MHz. As pointed out in the theoretical discussion, the usefulness of these relations is that they make possible the determination of the bond distances in a linear molecule by measurement of the rotational spectra of several isotopically-related species.

For this experiment, you will study the molecules **$^{16}O^{12}C^{32}S$** (the parent), **$^{18}O^{12}C^{32}S$**, **$^{16}O^{13}C^{32}S$**, and **$^{16}O^{12}C^{34}S$**. Each of the last three of these molecules differs from the parent by having one of the atoms isotopically substituted. If the frequency of a single rotational transition is measured for each of these species and the J quantum numbers are identified, the B_0 constants and moments of inertia can be calculated. From the moments of inertia of the parent and the **$^{18}O^{12}C^{32}S$**, the z-coordinate of the **O** atom can be calculated by equation above. From the moments of inertia of the parent and the **$^{16}O^{13}C^{32}S$**, the z-coordinate of the **C** atom can be determined. Finally, from the moments of inertia of the parent and the **$^{16}O^{12}C^{34}S$**, the z-coordinate of the S atom can be obtained. Then, since the **CO** bond distance is $z_C - z_O$ and the **CS** bond distance is $z_C - z_S$, it is easy to calculate these distances and fully determine the structure of the **OCS** molecule.

The determination of the structure of **OCS** is greatly simplified by the fact that the rotational spectra in this molecule are sufficiently intense (and sufficiently sparse) that the $J = 2 \leftarrow 1$ transition can be recorded for each of the four necessary isotopic species in their natural isotopic abundance (^{18}O: 0.20 %; ^{13}C: 1.11 %; ^{34}S: 4.22 %) in an ordinary sample. Thus, in this case, no isotopic labelling chemistry is required, as it has been historically for most molecules. The frequency of the $J = 2 \leftarrow 1$ transition in a linear molecule is just $4B_0$, from which the moment of inertia can be obtained by means of Equation (3). The masses of the isotopic species of the atoms are, as follows:

$m(^{16}O)$ = 15.9949 u ; $m(^{12}C)$ = 12.0000 u ; $m(^{32}S)$ = 31.9721 u

$m(^{18}O)$ = 17.9992 u ; $m(^{13}C)$ = 13.0034 u ; $m(^{34}S)$ = 33.9679 u

Procedure

1. Fill the sample cell with **OCS** to a pressure of 50 mTorr. Adjust the waveguide attenuator to set the crystal current to 50 μA.

2. Follow the operating instructions are included at the end of this write-up.

3. Set the Stark voltage to 800 V and set the synchronous detector time constant to 30 ms. The Stark voltage is modulated and synchronized in such a way that both the zero field and Stark shift peaks are seen in one spectrum. The peaks are 180° out of phase with each other, so it is easy to differentiate between the zero field and Stark shift peaks.

4. Record a spectrum for each of the following sets of conditions (the parameters are given here in the order that they appear in the SETUP menu in the MW472 program used to record the spectra: starting frequency/MHz, ending frequency/MHz, frequency interval/kHz, number of sweeps, integration number, timing number/ms, and delay number/ms). When the parameters are entered, the program will tell you the number of data points in each spectrum. Record this number – you will need it for the data analysis. Save each spectrum, as instructed by your TA.

   a) $\mathbf{^{16}O^{13}C^{32}S}$: 24242, 24252, 50, 1, 10, 30, 50.

   b) Set the synchronous detector time constant to 100 ms.

      $\mathbf{^{18}O^{12}C^{32}S}$: 22815, 22825, 50, 1, 10, 100, 50.

   c) Return the time constant to 30 ms for this spectrum.

      $\mathbf{^{16}O^{12}C^{34}S}$: 23725, 23735, 50, 1, 10, 30, 50.

   d) Reduce the sample pressure to 20 mTorr and the crystal current to 20 μA.

      $\mathbf{^{16}O^{12}C^{32}S}$: 24320, 24330, 50, 1, 5, 30, 50.

5. Leave the **OCS** in the system – it will be needed to calibrate the electric field spacing of the sample cell in the next part of the experiment.

<u>Part 2. The Determination of the Dipole Moment of NH_3 by means of the Stark Effect</u>

In this part of the experiment the dipole moment of ammonia will be determined by measuring the frequencies of two Stark components of a single transition in the inversion spectrum of ammonia at several different electric fields (ε). The electric field in the cell is determined by the applied voltage V and the distance between the positive and negative electrodes in the sample cell d ($\varepsilon = V/d$). The spacing d can be determined by measuring the Stark effect on a rotational transition of a molecule with a well-known dipole moment.

For this experiment the $J = 2 \leftarrow 1$ rotational transition in $\mathbf{^{16}O^{12}C^{32}S}$, which occurs at a frequency near 24,325.92 MHz in the absence of an electric field, will be used for determination of d. In the presence of an electric field that is parallel to the field of the microwave radiation, this transition splits into two components with M values of 0←0 and 1←1 (relative intensities 2:3; $M = |m|$). One component goes to higher frequency and the other to lower frequency following the equation:

$$\nu = \nu_R + \frac{(0.138095m^2 - 0.076190)\mu_0^2 V^2}{h^2 B_0 d^2}$$

where, ν is the frequency of the $m \leftarrow m$ Stark component in the applied field ε, ν_R is the frequency of the component in zero field, μ_0 is the dipole moment of the sample, h is Planck's constant, and B_0 is the rotational constant for the **OCS** species studied. (NOTE: This equation was derived specifically using the J and J' values for this transition. Your TA has information about the derivation, if you are interested.) Since the rotational frequency of a transition in a linear molecule in zero field is $2B(J+1)$, where J is the quantum number for the lower state, B_0 can be determined in this experiment by dividing the value of the zero-field frequency for the transition by four. The dipole moment of **OCS** has been measured very carefully, and is known to be 0.71215 ± 0.00020 D (J. S. Muenter, *J. Chem. Phys. 48*, 4544 (1968)). Some useful relationships for your calculations: 1D = 3.336 x 10^{-30} C·m and 1 V = 1 J/C.

After determination of the cell spacing, the sample cell is evacuated and a sample of $^{14}NH_3$ is introduced. The Stark effect of the (3,3) transition will be measured. This transition has three $M \leftarrow M$ Stark components in the presence of a field, one each for M = 1, 2, and 3. For J = 3, M can also equal 0, but the intensity of the $M = 0 \leftarrow 0$ transition is zero. All three M components go to higher frequency as the electric field is increased according to the equation,

$$\nu = \nu_R + \frac{(5.23673 \times 10^{-12}\, m^2)\mu_0^2 V^2}{h^2 d^2}$$

(Again, the derivation of this equation is available from your TA if you would like to see it.) Since the intensities of the Stark components are proportional to m^2, the relative intensities are 1, 4, and 9 for M = 1, 2, and 3, respectively. For this experiment, you will measure the frequencies of only the two strongest components (unless you want to measure the frequency of the weakest component as well). From the slope of a plot of the frequency of either component against V^2 and from the field spacing d determined from the Stark effect of **OCS**, the dipole moment of ammonia can be determined.

There is a complication in the spectrum of $^{14}NH_3$ that results from the fact that the ^{14}N nucleus has a non-zero positive value for the quadrupole moment, which means that the nucleus is a slightly-flattened sphere (like the earth). The rotational angular momentum (i.e., "spin") of the nucleus interacts with the rotational motion of the molecule, causing a splitting of the rotational transitions. Detailed calculations for the (3,3) line show that most of intensity is in the central line at the resonance frequency that would occur if there were no quadrupole coupling, but that there are two weak transitions on either side of the main transition separated from the main transition by about ±1.70 MHz and ±2.30 MHz (these should be barely seen in the spectrum). Fortunately, for our experiment, if the Stark shift in frequency is large compared to this splitting, the effect of the quadrupole coupling on the Stark effect may be ignored (the so-called "strong-field case"). This is easy to accomplish for the M = 2 and 3 components by making the frequency measurements in field above about 1 kV/cm (above about 500 V). It turns out, however, in this case that a plot of frequency against the square of the voltage cannot be reliably extrapolated back to zero to get the zero-field frequency.

Procedure

A. Determination of the electric field spacing in the sample cell.

The last spectrum of **OCS** collected in Part 1. of this experiment, is the first spectrum needed in the determination of the cell spacing. That spectrum was collected with a Stark voltage of 800 V. In order to determine the cell spacing, this spectrum must be recorded in the presence of a range of Stark voltages. Using the same parameters specified in 4.d. above, measure the spectrum of $^{16}O^{12}C^{32}S$ under each of the following Stark voltages: 500 V, 600 V, 700 V, and 900V.

B. Determination of the dipole moment of NH_3

1. Evacuate the sample cell. (Suggestion: while waiting for the **OCS** to be pumped from the cell, start fitting some of the data already collected. Instructions for curve fitting are given in the data analysis section of this write-up.)
2. Fill the cell with with NH_3 to a pressure of 40 mTorr.
3. Set the crystal current to 40 μA and the synchronous detector time constant to 30 ms. Record spectra for each of the 5 Stark voltages used for the **OCS** sample. Use the following conditions to start: 23865, 23905, 100, 1, 5, 30, 50. The two large Stark positive going lineshapes at higher frequency than the zero-field transition are the desired M = 2 and M = 3 Stark components. The conditions will have to be modified for higher Stark voltages because the Stark shift for NH_3 in these fields is much larger than for **OCS**. Set the frequency range to record the entire lineshapes of both of the two most intense Stark components (M = 2 and 3).

Data Analysis

Curve Fitting

A non-linear curve-fitting program: LLFITX will be used to fit the data in each spectrum. As with all curve-fitting, the program requires initial guesses of the parameters being fitted. The computer program VIEWFRQ will be used to do this.

1. Launch the program VIEWFRQ and choose a spectrum to analyze. Use the cross hairs to determine the spectroscopic baseline and the frequency, halfwidth at half height, and amplitude for the central transition. Record these in your notebook. F1 and F2 can be used to change the step size when the cursor is being moved around by the arrow keys. F3 allows you to bring up another spectrum and F4 closes the program.

Once you have determined the approximate values for the parameters for all spectra using VIEWFRQ, use the LLFITX program to perform a least-squares fit of each spectrum.

2. Launch LLFITX and enter the name of the file containing the spectrum to be fit (include the .GRA extension). You will be prompted to give an output file name for the fitted spectrum and then asked how many lines you are fitting to the data. Enter 1. You will then enter your the initial guesses for the 5 parameters being fitted. Enter them in the following order, on one line, with a space in between each and no commas:

   Background intensity   Background slope (1 – it's a horizontal background)   Frequency of main transition   Halfwidth at half height of main peak   Amplitude of main peak

When asked which parameters to fit enter: 1 1 1 1 1. All five parameters will then be varied until the best fit to the data is achieved. A reasonable value for the number of iterations is 15. When the program is doing the curve fitting, watch how the parameters are changed. If the parameters don't converge, then program will not be able to fit the data. This is usually easily fixed by either making better initial guesses or by holding some parameters fixed during the curve fitting process.

Once you have fit the curve, record the values of the fitted parameters and their errors in your notebook.

NOTE: When fitting the ammonia spectra, it is useful to fit only that part of the spectrum that includes the two Stark components.

Calculate the rotational constant *B* and the moment of inertia *I* for each OCS isotopic species. Then, calculate the z coordinate for each atom. Estimate the experimental uncertainy in each coordinate by using the standard error in the frequency obtained from the output of the LLFIT program.

Calculate the CO and the CS interatomic distances and estimate the experimental uncertainty in these values. The theoretical model that we have used to determine the interatomic distances by this method has a number of approximations that limit the accuracy of the distances obtained to ± 0.001 - 0.002 Å. Is this larger or smaller than your experimental uncertainty?

Using the data collected for OCS in Part 2. of the experiment, plot the frequencies of the two Stark components against the square of the applied voltage. Use the slopes of the lines and the known dipole moment of OCS to deduce the electric field spacing.

Using the data collected for ammonia and field spacing determined from the OCS spectra, calculate the dipole moment of ammonia.

Questions

Compare your structure of OCS to a literature value.

Compare your value of the dipole moment with a literature value of the dipole moment of the NH_3 molecule.

Operating the Spectrometer

1. Make sure that the sample cell is evacuated to a pressure below 5 mTorr
2. Load a sample of OCS or ammonia.
3. Perform the following:
    a) Turn off the enable switch on the computer interface.
    b) Set the switches on the sweep control to 24325.92 MHz for OCS or 23870 MHz for ammonia; push the reset on the sweep control. The frequency should show in the lights and the white light on the synchronizer should go out. If the synchronizer light does not go out, see the instructor.
    c) Increase the Stark base-to-peak voltage to about 800 V (if the fault light goes on, turn down the Stark voltage immediately; the sample pressure is probably too high).
    d) The lock-in amplifier should show a negative signal. Adjust the gain to keep the signal on scale without making it too small.
    e) Set the lock-in phase to 0°; adjust the fine phase control to bring the lock-in signal to zero.
    f) Set the lock-in phase to 180°; readjust the fine phase to bring the lock-in signal to zero. Repeat (e) and (f) to get the best compromise.
    g) Set the lock-in phase to 90° without touching the fine phase control.
    h) Turn on the enable switch on the computer interface.
4. To record a spectrum:
    a) Change directory on the computer to exp (CD \EXP)
    b) Type QB MW472<Enter>
    c) Use the right arrow key to move the cursor to HP K-R and press <Return>
    d) Adjust the spectroscopic conditions as desired; press Esc key.
    e) Put the cursor on Acquire; press <Enter> twice. The microwave frequency should start stepping on the computer screen and in the lights on the sweep control.
    f) After the spectrum is recorded, press <Enter>
    g) Put the cursor on Save; press <Enter>
    h) Type a 1-5 digit alphanumeric part of a file name, press <Enter>, and type a number from 001 to 999, and press <Enter>. For subsequent files the program will increment the file number, unless you want to change the name.
    i) Record additional files by putting cursor on Acquire and pressing <Enter> or by putting cursor on Setup and pressing <Enter> if you want change conditions.