

Microwave Spectroscopy

This experiment illustrates the use of molecular spectroscopic measurements for the determination of molecular properties. In particular, the study of the rotational spectrum of a linear triatomic molecule, OCS, permits a determination of a variety of molecular constants including the bond lengths and dipole moment.

Theory

Rotational Spectra

Consider the linear triatomic molecule OCS given in Fig. 1. The atoms have masses m_O , m_C , and m_S , and are separated by the bond lengths r_{CO} and r_{CS} . Rotational motion for this molecule involves rotation of the molecular axis about the center-of-mass (COM). The positions z_O , z_C , and z_S of the atoms measured from the center-of-mass (COM) are given by

$$m_O z_O + m_C z_C + m_S z_S = 0 \quad (1)$$

and the bond lengths can be expressed in terms of the atomic positions:

$$r_{CO} = z_C - z_O \quad (2)$$

$$r_{CS} = z_S - z_C \quad (3)$$

If the molecule is approximated as a linear rigid rotor then the moment of inertia, I , for rotation about the COM is given by

$$I = m_O z_O^2 + m_C z_C^2 + m_S z_S^2 \quad (4)$$

The corresponding kinetic energy, according to classical mechanics, is

$$T = \frac{1}{2} I \omega^2 \quad (5)$$

where ω is the angular velocity of rotation (radians/sec). The angular momentum is

$$J = I \omega \quad (6)$$

in terms of which the kinetic energy of rotation is

$$T = \frac{J^2}{2I} \quad (7)$$

In the absence of external fields, there is no potential energy term for the rigid molecule.

According to quantum mechanics, the energy is still given by Eq. 7, but the angular momentum is quantized. The eigenfunctions of the square of the angular momentum, J^2 , are the spherical harmonics, which obey the eigenvalue equation,

$$J^2 Y_{JM}(\theta, \varphi) = J(J+1) \hbar^2 Y_{JM}(\theta, \varphi) \quad J = 0, 1, 2, \dots \quad (8)$$

The angular coordinates θ and φ are defined with respect to the laboratory-fixed coordinate system as shown in Fig. 2, and the component of angular momentum along the laboratory fixed z -axis has its own eigenvalue equation

$$J_z Y_{JM}(\theta, \varphi) = M \hbar Y_{JM}(\theta, \varphi) \quad M = -J, -J+1, \dots, J-1, J \quad (9)$$

Since the energy operator (Hamiltonian) is proportional to J^2 , each pair of allowed values for J and M corresponds to a stationary state for the rotor. The energy of the stationary state JM is, from Eqs. 7 and 8, given by

$$E_{JM} = h B J(J+1) \quad (10)$$

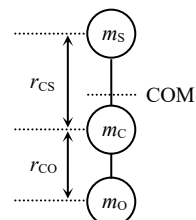


Figure 1. General layout of a linear triatomic molecule. The precise location of the COM depends on the masses and bond lengths.

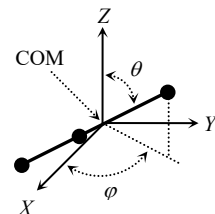


Figure 2. Definition of the angles specifying the orientation of the linear rotor.

The probability density that the molecule in state JM has its axis described by θ, φ is

$$|Y_{JM}(\theta, \varphi)|^2$$

To help visualize any specific spherical harmonic, Y_{JM} , start with a sphere and note that: 1) J corresponds to the total number of nodes passing through the sphere, 2) $|M|$ corresponds to the number of longitudinal nodal planes that contain the z -axis, and 3) $J-|M|$ corresponds to the number of nodal surfaces (not necessarily planes) passing through the z -axis at the origin. Also note that these same spherical harmonics are used to describe atomic orbitals.

where B is called the rotational constant, and expressed in units of Hz is given by

$$B = \frac{h}{8\pi^2 I} \quad (11)$$

An applied electromagnetic field can stimulate electric dipole transitions between the stationary states causing the molecule to either absorb or emit a photon in the process. In general a transition from state JM to state $J'M'$ can occur if the energy of a photon of the field matches the energy level difference between the two energy levels ($\Delta E = h\nu$) and the transition dipole (μ_{tr}) is non-zero, as shown below:

$$\mu_{tr} = \int_0^\pi \int_0^{2\pi} Y_{JM'}^*(\theta, \varphi) \hat{\mu} Y_{JM}(\theta, \varphi) \sin \theta d\theta d\varphi \quad (12)$$

In this experiment the applied field is linearly polarized along the laboratory fixed z -axis so only interaction with the z -component of the electric dipole moment, $\mu_z = \mu \cos \theta$, can lead to transitions. With the realization that $\cos \theta \propto Y_{10}$ and substituting into Eq. 12 produces the following triple integral:

$$\mu_{tr} \propto \mu \int_0^\pi \int_0^{2\pi} Y_{JM'}^*(\theta, \varphi) Y_{10} Y_{JM}(\theta, \varphi) \sin \theta d\theta d\varphi \quad (13)$$

When the integral is evaluated it is found that the selection rules for allowed transitions are

$$\mu \neq 0 \quad \Delta J = \pm 1 \quad \Delta M = 0 \quad (14)$$

Molecular Vibrations

Eq. 10 is the solution for the energy levels for a rigid linear rotor. A linear molecule behaves similar to this model, but a molecule is not rigid; the individual atoms are bound by flexible bonds and are in constant motion due to molecular vibrations. A linear triatomic molecule such as OCS has 4 vibrational modes: a symmetric stretch, an asymmetric stretch, and two degenerate bending modes perpendicular to each other. Since the vibrational motion is substantially faster than the rotational motion, it is reasonable to model the rotation as occurring with a single vibrationally-averaged rotational constant, B_v :

$$B_v(v_1, v_2, \dots, v_N) = B_e - \sum_{i=1}^N \alpha_i (v_i + d_i / 2) \quad (15)$$

$B_v(0,0,0)$ is often referred to as B_o

where i is the index of the normal mode, α_i is the vibration-rotation interaction constant, v_i is the vibrational quantum number, and d_i is the degeneracy. Specifically, for the ground vibrational state ($v_i = 0$ for all modes) the vibrationally-averaged rotational constant is simply called the observed rotational constant and is given the symbol B_o . The sign of α depends on the character of the normal mode. For example, the anharmonicity in the potential of stretching modes causes the average nuclear positions to be slightly farther apart than the equilibrium positions, meaning that $I_v > I_e$, $B_v < B_e$, and $\alpha > 0$. For OCS, Eq. 15 can be written as

$$B_v(v_1, v_2, v_3) = B_e - [\alpha_1(v_1 + 1/2) + \alpha_2(v_2 + 1) + \alpha_3(v_3 + 1/2)] \quad (16)$$

Values for α_i can be determined from the rotational constants of molecules in known vibrational states using Eq. 16. For example, α_1 can be determined from $B_v(1,0,0)$ and B_o as

$$B_o - B_v(1,0,0) = (B_e - B_e) - \left[\left(\frac{\alpha_1 + 2\alpha_2 + \alpha_3}{2} \right) - \left(\frac{3\alpha_1 + 2\alpha_2 + \alpha_3}{2} \right) \right] = \alpha_1 \quad (17)$$

Experimental determination of all the B_v values necessary to determine values for α_1 , α_2 , and α_3 is not possible with the apparatus used in this experiment due to the low population of the vibrationally-excited states. Because of this the α coefficients will be calculated from literature data and used to convert B_o values to B_e values.

Determination of Structure from Isotopic Substitution Data

Determination of bond lengths from the measured transition frequencies stems from determining B from spectroscopic measurements and subsequently I . Eqs. 1-4 relate the molecular structure to the moment of inertia. However, upon inspecting the set of equations it is evident that the data set is underdetermined (too many variables relative to the number of equations) and does not describe a unique combination of internuclear distances. Specifically, there are three variables (z_O , z_C , and z_S) but only two equations (Eqs. 1 and 4). If the $^{16}\text{O}^{13}\text{C}^{32}\text{S}$ molecular isotope is included, then the following two equations are added to the set:

$$I' = m_O z_O'^2 + m_C' z_C'^2 + m_S z_S'^2 \quad (18)$$

$$m_O z_O' + m_C' z_C' + m_S z_S' = 0 \quad (19)$$

where m_C' is the mass of the ^{13}C isotope. Initially this may not appear helpful since three new unknowns are added (the three atomic coordinates) with only two equations, but a key assumption is that the equilibrium bond lengths are the same for all molecular isotopes. With this assumption it is evident that an isotopic substitution will result in changes to all three coordinates of the atoms, but the differences between the coordinates will stay the same (i.e., all atoms will have their coordinates shifted by the same amount, Δz). Thus, the z' values are related to the z values in Eqs. 1 and 4 by

$$z_O' = z_O + \Delta z \quad z_C' = z_C + \Delta z \quad z_S' = z_S + \Delta z \quad (20)$$

So adding a molecular isotope to the data set only adds one unknown (Δz) and two equations. This means the data set is fully determined, although with zero degrees of freedom, by using two isotopes. The data set becomes overdetermined if more than two isotopes are used. This is analogous to using, say, three points to determine a line instead of only two.

In this experiment you will combine data from a total of three molecular isotopes: 1) $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ (primary isotope), 2) $^{16}\text{O}^{13}\text{C}^{32}\text{S}$, and 3) $^{16}\text{O}^{12}\text{C}^{34}\text{S}$. The sample is naturally abundant, so all molecular isotopes are present at relative concentrations consistent with the natural abundance of the atomic isotopes (e.g. $^{16}\text{O}^{13}\text{C}^{32}\text{S}$ is present as 1.1% of the entire sample). Analogous to finding the best-fit line amongst three points, the best-fit bond lengths come from minimizing the sum of the square of the residuals (SSR) of the rotational constants:

$$SSR = \sum_i (B_i - B_{\text{fit},i})^2 \quad (21)$$

where B_i is an experimentally determined rotational constant and $B_{\text{fit},i}$ is a rotational constant from the structure (equations like 4 and 18). A simple approach is to use the Excel Solver add-in to minimize the SSR by modifying the bond lengths. A sample spreadsheet is shown below:

Calculations from experimental data

Isotope mass / amu

^{16}O

15.99491462

^{12}C

12.00000000

^{13}C

13.00335484

^{32}S

31.97207100

^{34}S

33.96786690

Constants

h

6.626E-34

J-s

m_u

1.661E-27

kg

Exp abs freqs / MHz

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$

24325.879

$^{16}\text{O}^{12}\text{C}^{34}\text{S}$

23731.282

$^{16}\text{O}^{13}\text{C}^{32}\text{S}$

24247.667

B / MHz

Vib-Ave (B_v)

Eq (B_e)

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$

6081.470

6099.407

$^{16}\text{O}^{12}\text{C}^{34}\text{S}$

5932.821

5950.169

$^{16}\text{O}^{13}\text{C}^{32}\text{S}$

6061.917

6079.385

$r_e(\text{CO}) / \text{pm} = 115.388$

$r_e(\text{CS}) / \text{pm} = 156.326$

α coefficients / MHz

α_1

α_2

α_3

total

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$

36.44

-9.35

18.14

17.94

$^{16}\text{O}^{12}\text{C}^{34}\text{S}$

35.45

-9.22

17.69

17.35

$^{16}\text{O}^{13}\text{C}^{32}\text{S}$

34.28

-8.66

17.98

17.47

z / pm

O

C

S

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$

-167.958

-52.570

103.756

$^{16}\text{O}^{12}\text{C}^{34}\text{S}$

-171.300

-55.912

100.414

$^{16}\text{O}^{13}\text{C}^{32}\text{S}$

-167.093

-51.705

104.621

I / (amu·pm²)

fit

exp

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$

828567.5

6099.431

6099.407

0.0005

$^{16}\text{O}^{12}\text{C}^{34}\text{S}$

849360.9

5950.109

5950.169

0.0036

$^{16}\text{O}^{13}\text{C}^{32}\text{S}$

831294.7

6079.420

6079.385

0.0013

SSR =

0.0054

Note that the z values are calculated from the bond lengths using Eqs. 1-3 (and analogous equations for the various molecular isotopes).

A key assumption in the analysis is that the equilibrium bond lengths are the same for all isotopic species. This stems from the Born-Oppenheimer approximation which separates the motion of electrons from the motion of nuclei. Think about the physical basis for this approximation.

Determination of Dipole Moment from the Stark Effect

The *Stark effect* is the change in frequency of an absorption line because of an external electrostatic field. This effect can be used to determine the electric dipole moment, μ , of the molecule. Recall that for an assembly of point charges μ is defined by

$$\mu = \sum_i q_i r_i \quad (22)$$

Note that in practice, $E = V/d$ where d is the spacing between the Stark electrode and the wall of the waveguide.

where r_i is the vector position of charge q_i . When an electrostatic field, \mathcal{E} , is applied along the laboratory fixed z -axis, the energy term arising from the interaction of the dipole with the field is

$$-\mu \cdot \mathcal{E} = -\mu \mathcal{E} \cos \theta \quad (23)$$

This is added to the rotational energy of the state given by Eq. 10. The quantum mechanical problem of finding the stationary state energy values is difficult to solve exactly, but a very satisfactory procedure is to develop the energy as a power series. The linear term vanishes exactly (i.e., $E_{JM}^{(1)} = 0$), and the result given by the quadratic term is

$$E_{JM}^{(2)} = \mu^2 \mathcal{E}^2 \left(\frac{\left(\frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \right)}{E_J - E_{J+1}} + \frac{\left(\frac{J^2 - M^2}{(2J-1)(2J+1)} \right)}{E_J - E_{J-1}} \right) \quad (24)$$

Note that the selection rules of Eq. 14 continue to hold because in the apparatus used the electrostatic field and the microwave electric field are both polarized along the same direction.

Conceptually Eq. 24 describes that the state JM gets perturbed by the states $(J+1)M$ and $(J-1)M$. This can be described classically as the molecular dipole accelerating as it moves towards the direction of the field, mixing in the $(J+1)M$ state, and decelerating as it moves away from the direction of the field, mixing in the $(J-1)M$ state. It can be said that energy states repel each other; since $E_J - E_{J-1}$ is positive, interaction with the $(J-1)M$ state raises the energy of the JM state and since $E_J - E_{J+1}$ is negative, interaction with the $(J+1)M$ state lowers the energy of the JM state. Depending on the relative magnitudes of these two effects the net change to the energy of the JM state could be positive or negative. Also note that the magnitude of the shift is inversely proportional to the energy level differences; since the energy level spacing increases with increasing J , the magnitude of the Stark shift also decreases with increasing J . Eq. 24 can be reduced further to

$$\begin{aligned} E_{JM}^{(2)} &= -\frac{\mu^2 \mathcal{E}^2}{6hB} \quad (J=0) \\ &= -\frac{\mu^2 \mathcal{E}^2}{2hB} \left(\frac{3M^2 - J(J+1)}{J(J+1)(2J-1)(2J+3)} \right) \quad (J>0) \end{aligned} \quad (25)$$

Note that $\mathcal{E} = V/d$ where d is the spacing between the Stark electrode and the wall of the waveguide.

The Debye unit, commonly used for molecular dipole moments, is equivalent to 3.3356×10^{-30} C·m.

This is accurate enough for most experimental work. In the presence of electromagnetic fields of appropriate frequency, the selection rules of Eqs. 14 continue to hold because in the apparatus used, the electrostatic field and the microwave electric field are both polarized along the same direction. Note that Eq. 25 is a correction to the description of the energy levels given by Eq. 10. For example, calling the energy given by Eq. 10 as $E_{JM}^{(RR)}$ (for rigid rotor), the energy level for state JM under the influence of a Stark shift is given by

$$E_{JM} = E_{JM}^{(RR)} + E_{JM}^{(2)} \quad (26)$$

Practical Matters

Microwave Waveguides

The microwave region of the electromagnetic spectrum spans the range of 3 - 300 GHz which lies between the ultrahigh frequency (UHF) region and the far infrared region. The practical reason for distinguishing these regions is that rather different experimental techniques are used for transmitting electromagnetic energy for each of them. Ordinary electronic circuit techniques (based on the use of resistors, capacitors, inductors, transistors, and wire conductors) begin to fail badly at the upper end of the UHF frequency band where the wavelength becomes comparable to the dimensions of the circuit elements. Standard optical methods, on the other hand, work best when the wavelength is much smaller than the dimensions of the laboratory elements (e.g., gratings, lenses, and sample cells) that are used; these methods are not very convenient at frequencies below the lower end of the infrared region. Microwave radiation is most efficiently transmitted through *waveguides*, which are metal tubes of rectangular cross section, with the broad side usually chosen to be between 0.5 and 1 times the wavelength of the radiation transmitted.

Propagation of microwave radiation through the waveguide occurs differently than propagation through free space, which is generally described using a transverse electric and magnetic (TEM) mode. This means that the electric field and the magnetic field are both perpendicular to the direction of propagation, and perpendicular to each other. However, when constrained to a waveguide, this mode of propagation is not allowed and propagation occurs with modes that are either transverse electric (TE) or transverse magnetic (TM). In this experiment it is the TE mode that is of interest since the effect under investigation involves the electric field of the microwave radiation interacting with the electric dipole of the molecule. In this mode of propagation the electric field is polarized so that it is perpendicular to the broad side of the waveguide. For this reason the fixed laboratory *z*-axis is defined as this same direction. Further details (and illustrations) about the propagation of microwave radiation are provided in the supplemental materials on the course website.

Microwave Spectrometer

The components of the microwave spectrometer are shown below in Fig. 4:

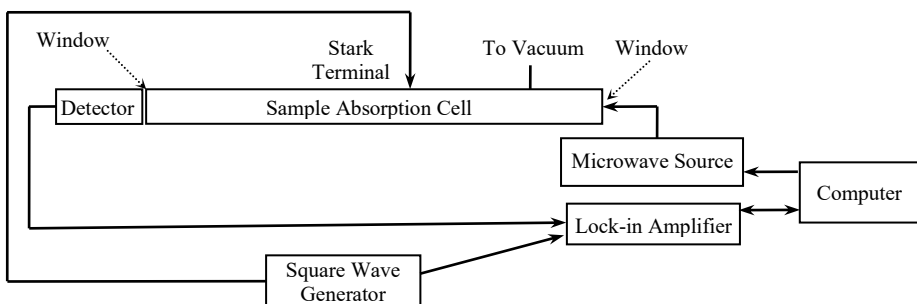


Figure 4. Schematic of the microwave spectrometer used in this experiment.

The absorption cell consists of a section of waveguide, about 8 ft. in length, sealed off with a thin mica window at each end and is vacuum tight. To provide a means of removing air and introducing sample gases, the cell is connected to the glass vacuum manifold. Additional small sections of microwave waveguide connect the cell to the microwave source at one end and to a zero bias Schottky diode detector at the other. To permit application of electric fields to the sample, the cell is constructed with an electrode strip parallel to the broad side and extending almost the entire length of the cell. This electrode is supported by two grooved strips of Teflon tape, so that it is well insulated from the waveguide walls. Near one end, the electrode is connected to an electrical lead, in the form of a metal pin which passes through a vacuum tight metal and glass feed through. The glass provides electrical insulation between the pin and the waveguide walls. By application of a voltage between the electrode and the outside walls of the waveguide, a field is produced which is reasonably uniform over the volume of the sample cell. The cell may be thought of as approximating a parallel-plate capacitor. A cutaway portion of the Stark cell, showing the details of construction, is available for examination. Note that the spacing between the electrode and the outer wall is 4.64 mm.

The waveguide used in the present experiment has cross sectional dimensions of 1"×1/2" and is designed for use throughout the frequency range 8.0 - 12.4 GHz, which corresponds to a wavelength range 3.7 - 2.4 cm.

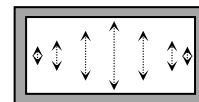


Figure 3. Electric field lines in a waveguide for electromagnetic radiation propagated in a TE mode. Note that the electric field is polarized in the direction of the broad face, which is defined as the laboratory *z*-axis.

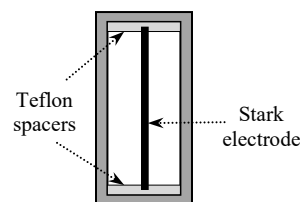


Figure 5. Position of the Stark electrode inside the waveguide.

The detector produces an electrical signal proportional to the microwave power. If the sample absorbed a large fraction of the incident microwave power, the absorption spectrum could be observed by simply scanning over the frequency range and watching for dips in the detector response. However, the fraction absorbed by the sample gas is less than 10^{-6} even for relatively strong lines. Much larger changes result from variations in the output power of the microwave source, and variations in the transmission characteristics of the absorption cell, producing an irregular baseline which overshadow the changes due to a molecular absorption line. So instead of directly monitoring the detector output, the signal is modulated by the Stark effect and a lock-in amplifier is used to isolate it.

Lock-in Amplification

Sample absorption of the microwave source is much too small relative to the noise to measure directly so a lock-in amplifier is used to make the measurement. Lock-in amplifiers provide substantial noise reduction which leads to an increase in the signal-to-noise ratio (S/N) on the order of about 10^5 . Many measurements would simply be impossible without the large gain in S/N provided by lock-in detection, and it is used in many applications you see every day but might not be aware of. For example, the sensors used as a safety feature on garage doors discriminate the tiny signal of a LED relative to the large amount of stray light striking the photodiode through lock-in amplification.

A lock-in amplifier requires an *input* and a *reference*. The input contains the noisy signal to be measured and the reference contains the frequency of the pure signal. The lock-in amplifier then performs three functions in order: 1) the input and reference are multiplied together, 2) the result is sent through a low-pass filter, and 3) that result is then amplified to a level where it can be measured directly. For output, the lock-in amplifier has two channels X and Y . Let's analyze each step and focus on the pure signal, represented as $V_s \sin(\omega_s t + \phi_s)$, and the reference, represented as $V_r \sin(\omega_r t + \phi_r)$ for the X -channel output. Multiplying the two together produces:

$$V_s \sin(\omega_s + \phi_s) V_r \sin(\omega_r + \phi_r)$$

$$\frac{1}{2} V_s V_r [\cos(\{\omega_s - \omega_r\}t + \{\phi_s - \phi_r\}) - \cos(\{\omega_s + \omega_r\}t + \{\phi_s + \phi_r\})]$$

Thus, multiplying sine waves results in components that are the sum of the two frequencies and the difference between the two frequencies. Since $\omega_s = \omega_r$, the difference of the frequencies is zero and that term loses its time dependence. The low-pass filter removes terms with a time dependence, resulting in:

$$\frac{1}{2} V_s V_r \cos(\Delta\phi)$$

Lastly, amplification by some gain, G , produces the output of the X -channel, V_X :

$$V_X = \frac{1}{2} G V_s V_r \cos(\Delta\phi) \Rightarrow V_X \propto V_s \cos(\Delta\phi)$$

For the Y -channel, the reference is phase-shifted by 90° , which results in a similar response:

$$V_Y \propto V_s \sin(\Delta\phi)$$

So, both channels produce a response that is proportional to the amplitude of the pure signal (V_s) and the phase difference between the signal and reference ($\Delta\phi$). This can be represented geometrically in two-dimensions:

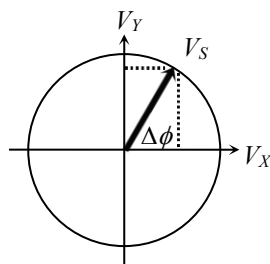


Figure 6. Two-dimensional representation of the V_X and V_Y output voltages of a lock-in amplifier measuring a signal V_s with a phase difference of $\Delta\phi$.

It is evident from the figure above that the total response of the lock-in amplifier is split between the two channels. When making measurements it is optimal to have a maximum response in one channel (resulting a minimum response in the other channel), so lock-in amplifiers have a phase adjustment parameter that can be added to the value of $\Delta\phi$.

The discussion above focused on the pure signal, but the entire reason for performing lock-in amplification instead of a direct measurement is because of the relatively large amount of noise present with the signal. So, what happens to the noise during the process of lock-in amplification? Noise occurs at all frequencies, but unless it matches the frequency of the signal then both the sum and difference terms in the multiplication step above have a time dependence and both are removed by the low-pass filter. The key is then to choose a reference frequency where the noise at that frequency is minimal. One of the “quiet” regions in the EM background is between 1-100 kHz, so most chemical instruments use frequencies in this range. Specifically, 50 kHz is chosen as the reference frequency for this spectrometer.

The two main questions that remain are: 1) How is the signal modulated at 50 kHz? and 2) What is V_s in this application? In this application we use the Stark effect to modulate the signal at 50 kHz. Applying a static electric field to the sample cell effectively changes the color of the sample (see Fig. 7 for an example). Switching this field on and off causes the power seen at the detector to oscillate at the same frequency. This is accomplished with the square wave generator, which applies a 50 kHz, zero-based square wave voltage to the Stark electrode of the sample cell. The 50 kHz timing is also sent to the lock-in amplifier as the reference frequency. So the strength of the signal, V_s , is the difference in microwave power between when the Stark field is on and when it is off. Mathematically this can be represented as:

$$V_s = V_{on} - V_{off}$$

where V_{on} is the detector voltage when the field is on and V_{off} is the detector voltage when the field is off. Consider a microwave frequency that does not match the absorption frequency when the field is on or off; in this case $V_{on} = V_{off}$ and $V_s = 0$. Now consider a microwave frequency that matches the absorption frequency when the field is off; V_{off} is less than V_{on} , because some of the microwave power is absorbed by the sample, and V_s is positive. Lastly, consider a microwave frequency that matches the absorption frequency when the field is on; V_{on} is then less than V_{off} and V_s is negative. Now because the choice of phase is arbitrary this does not mean that the Stark-shifted absorption frequencies must appear with negative intensity and the unshifted frequencies must appear with positive intensity, but it does mean that the Stark-shifted absorption frequencies will always appear with the opposite sign as the unshifted frequencies.

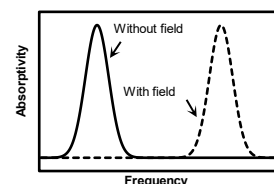


Figure 7. Shift of absorption frequency for $J=0 \rightarrow 1$ due to Stark effect.

Literature Values

Note that the precision in the experiment is quite high (7+ significant figures) so do not round any of the literature values.

$$h = 6.626070040 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$\text{amu} = 1.660539040 \times 10^{-27} \text{ kg}$$

<i>Isotope</i>	<i>mass / amu</i>
^{16}O	15.99491462
^{12}C	12.00000000
^{13}C	13.00335484
^{32}S	31.97207100
^{34}S	33.96786690

From *Maki, J. Phys. Chem. Ref. Data*, 3, 1974:

$$r_e(\text{CS}) = 156.28 \text{ pm}$$

$$r_e(\text{CO}) = 115.43 \text{ pm}$$

$$\mu = 0.71519 \text{ D}$$

<i>Molecule</i>	<i>Vib. State</i>	<i>B_v / MHz</i>
$^{16}\text{O}^{12}\text{C}^{32}\text{S}$	(0,0,0)	6081.492439
	(0,2 ⁰ ,0)	6100.19116
	(0,0,1)	6063.35744
	(1,0,0)	6045.051
$^{16}\text{O}^{12}\text{C}^{34}\text{S}$	(0,0,0)	5932.8379
	(0,2 ⁰ ,0)	5951.273
	(0,0,1)	5915.152
	(1,0,0)	5897.390
$^{16}\text{O}^{13}\text{C}^{32}\text{S}$	(0,0,0)	6061.92498
	(0,2 ⁰ ,0)	6079.250
	(0,0,1)	6043.949
	(1,0,0)	6027.649

Day 1 Checklist

Preparation

- ☐ Read the handout.
- ☐ Watch the videos listed under the “Day 1 Videos” section on the course website.
- ☐ Complete online quiz #1.

Activities

1.1. *Energy levels and spectroscopic transitions:* Sketch an energy level diagram for the $J = 0, 1$ and, 2 stationary states using Eq. 10 and sketch the wavefunctions. Note the position of each energy level as well as the spacing between them (in terms of B and in units of MHz). Note the transitions allowed in the experiment. Derive an expression for the frequency of a photon required to induce a transition from J to $J+1$ using Eq. 10. Demonstrate the equation matches the energy level spacing determined in the previous exercise.

1.2. *Understanding the Stark effect:* Calculate the values for c_{JM} in the expression:

$$E_{J|M|}^{(2)} = c_{JM} \left(\frac{\mu^2 E^2}{hB} \right) \text{ using } J = 0-2 \text{ and } |M| = 0-2 \text{ and Eq. 25. Make a sketch similar to the}$$

first exercise to show the effect of applying an external static electric field to the system; include the allowed transitions and note the frequency shift (positive or negative) in each transition relative to when there is no applied electric field. Compare the relative magnitude of the shifts for each transition at each level of J .

1.3. *Understanding an experimental spectrum:* You will use the *Microwave Simulator* spreadsheet on the course website for this activity. Start with 60 mtorr of sample, 400 V for the Stark voltage, 0 degrees for the phase, and a scan range of 12160 MHz to 12170 MHz. This range is appropriate to record the absorption frequency of the primary isotope of OCS for the $J = 0 \rightarrow 1$ transition. Don't be concerned about the phase of the spectrum for now, meaning whether peaks appear with a positive or negative intensity. Correlate the observed features with your plots of the energy levels and Stark shifts from the previous activities. Play around with the sample pressure and the Stark voltage and observe the impact of each parameter on the spectrum. Ask questions! Change the frequency range to be appropriate for the $J = 1 \rightarrow 2$ transition and correlate the spectrum with the energy level diagrams sketched previously. Discuss your observations.

1.4. *Understanding phase:* Fig. 6 shows the output voltage of each channel when measuring a signal with a given phase relationship. As discussed in the handout, in this application the Stark-shifted signals have a 180° relationship with the unshifted signals, so you could make a modified sketch of Fig. 6 that has signal arrows 180° apart from each other to represent this. Try different values for the phase, collect spectra, and correlate the results with the two-dimensional representation. Find values for the phase that result in maximum values for V_X , and those that result in maximum values for V_Y . Lastly, determine the value of $\Delta\phi$ in this case (recall that the convention is V_s is positive for the unshifted signals).

1.5. *Understanding digital resolution:* Although the spectrum may appear as a continuous signal it is actually comprised of 500 discrete measurements. Those discrete measurements are then displayed using a simple “connect the dots” approach. The density of the measurements is called the *digital resolution*. Set the sample pressure to 60 mtorr, the Stark voltage to 400 V, and set the phase to an appropriate value (determined in the previous activity). Collect a spectrum using a scan range of 12162 MHz to 12164 MHz. Calculate the digital resolution of this spectrum, in units of pts/MHz. Copy the data into a different set of cells in the spreadsheet to save the spectrum. Collect a new spectrum using a scan range of 12162 MHz to 12362 MHz and determine the digital resolution. Overlay the two spectra on the same plot with a display range of 12162 MHz to 12164 MHz. Discuss the impact of digital resolution on the location of the apparent signal maximum.

Day 2 Checklist

- 2.1. *Signal-to-noise*: The signal-to-noise ratio, S/N , quantifies the sensitivity of a spectrum. It is calculated by taking the intensity of the signal divided by the standard deviation (σ) of the random fluctuations in the measurement (i.e. the “noise”). Recall that 99.7% of a normal distribution curve is encompassed $\pm 3\sigma$. Therefore, σ can be estimated from a reasonable number of measurements (approximately 100+) by taking the range of observed values and dividing by 6. In particular for this experiment, this process is best done by taking a spectrum of just noise (no signals) near the frequency of the signal of interest.

Determine the S/N for the unshifted peak of the $J = 1 \rightarrow 2$ transition for the primary isotope using a pressure of 60 mtorr, a Stark voltage of 1000 V, and an appropriate value for the phase.

Use the S/N value determined above to predict the S/N for the same peak of ^{34}S and ^{13}C molecular isotopes. Explain whether you expect these to be measurable. Acquire a spectrum of each molecular isotope to verify your predictions.

- 2.2. *Coadding scans*: In the previous activity you determined that observation of the ^{13}C molecular isotope is not possible with a single scan. Recall from Chem 563 that precision can be improved through multiple measurements. Specifically, when adding numbers together

$$\sigma_T = \sqrt{\sigma_1^2 + \sigma_2^2 + \dots}$$

where σ_T is the total combined standard deviation, and σ_i is the standard deviation for each measurement. In the case of combining N replicate scans, the standard deviation of each measurement is the same, thus $\sigma_T = \sqrt{N}\sigma$. Also, the signal for each measurement, S_i , is the same, so the combined signal from adding N scans is given by $S_T = NS$. This means that the signal-to-noise ratio improves at a rate of $S_T / \sigma_T = (N / \sqrt{N})(S / \sigma) = \sqrt{N}(S / \sigma)$.

Choose an appropriate sample pressure and calculate how many spectra must be coadded together to achieve a spectrum with a $S/N = 5$ (considered the detection limit) for the ^{13}C isotope.

Although you could copy+paste individual scans into separate columns and add them together, it is much more productive to automate this task in the form of a macro. The first modification to make is to add a field for the number of scans. Use cell B7 to store the value, and use cell A7 to label it. Next, open the Visual Basic editor from the Developer tab (you may need to add this tab to your menu bar) and add this subroutine at the end of the programming module (after the GenerateSpectrum subroutine):

```
Public Sub CoaddScans()  
    Dim CoaddedX(502) As Double  
    Dim CoaddedY(502) As Double  
    Dim nscans As Integer  
    Dim i As Integer  
    Dim j As Integer  
  
    nscans = Range("B7").Value2  
  
    For j = 3 To 502  
        CoaddedX(j) = 0#  
        CoaddedY(j) = 0#  
    Next j  
  
    Application.ScreenUpdating = False  
  
    For i = 1 To nscans  
        GenerateSpectrum  
  
        For j = 3 To 502  
            CoaddedX(j) = CoaddedX(j) + Cells(j, 7).Value2  
            CoaddedY(j) = CoaddedY(j) + Cells(j, 8).Value2  
        Next j  
    Next i  
  
    Application.ScreenUpdating = True  
  
    For j = 3 To 502  
        Cells(j, 7).Value2 = CoaddedX(j)
```

```

Cells(j, 8).Value2 = CoaddedY(j)
Next j

End Sub

```

You may not be familiar with the details of macro programming, but you can probably get the basic idea from reading it. The general process is:

- 1) set up variables
- 2) retrieve the # of scans stored in B7
- 3) zero the coadded data set
- 4) for as many scans requested, acquire a scan and add the data to the current coadded data
- 5) overwrite the single spectrum data with the coadded data

Your new macro can be run by either selecting it from the Macros menu under the Developer tab, or by editing the Scan button and changing the assigned macro from GenerateSpectrum to your new subroutine, CoaddScans.

Test functionality of your spreadsheet and macro by acquiring a coadded spectrum of the ^{13}C isotope with the number of scans you calculated to obtain a $S/N = 5$. Submit your calculations for the number of scans to attain $S/N = 5$, a single scan spectrum of the ^{13}C isotope, and a coadded scan spectrum of the ^{13}C isotope with $S/N = 5$. Demonstrate that both the observed signal and noise match expectations for coadding replicate scans.

- 2.3. *Line shape*: From the energy level diagrams sketched during the Day 1 activities you might expect the spectrum to consist of signals that are near infinitely narrow; however, the signals are broadened from a variety of effects. In this experiment the main types of broadening are instrumental, Doppler, and collisional. Instrumental broadening comes from random variations inherent in the instrument. For example, the Stark plate is not perfectly aligned throughout the entire waveguide. These random variations typically result in a Gaussian line shape that is independent of experimental conditions like temperature and pressure. Doppler broadening occurs because the molecules are in motion relative to the microwave source. Molecules moving towards the source see a higher frequency (blue-shifted) vs. those moving away from the source see a lower frequency (red-shifted). Therefore, a range of frequencies from the microwave source will be absorbed. This type of broadening only depends on temperature and leads to a Gaussian distribution. Since the temperature is constant in this experiment, the amount of Doppler broadening is constant regardless of other settings, such as pressure. Collisional broadening can be the result of a few different mechanisms. One mechanism is that collisions may lead to minor perturbations in the energy levels. Another important mechanism is that collisions may reduce the lifetime of absorption and emission processes. This type of broadening depends on temperature and pressure and leads to a Lorentzian distribution.

The total amount of signal (i.e. the area of the signal) is proportional to the pressure of the sample, but the height of the signal is a bit more complicated because of the various sources of broadening. In the absence of collisional broadening the signal height is proportional to the pressure because the amount of broadening is constant. In the limiting case of only collisional broadening the signal height is nearly unchanged by the pressure because although the area increases, the broadening also increases by about the same amount.

Explore this pressure effect by measuring the signal height and the signal width (as FWHM, full-width at half-maximum) for pressures between 2 and 500 mtorr. Use at least 8 measurements and note that it is not a linear dependence so you should use more points in the lower pressure region. As with the previous activity, measure the unshifted peak of the $J = 1 \rightarrow 2$ transition for the primary isotope, a Stark voltage of 1000 V, and an appropriate value for the phase. Make a plot of the signal height vs. pressure, and the signal width vs. pressure. Write a short summary (a few sentences) about suitable choices for pressure when making measurements.

Day 3 Checklist

Preparation

- ☐ Watch the videos listed under the “Day 3 Videos” section on the course website.
- ☐ Complete online quiz #2.

Activities

3.1. Determining the dipole moment:

- a)** Develop a method to determine μ from the Stark-shifted frequencies of the $J = 1 \rightarrow 2$ transition using a linear equation ($y = mx + b$) where “ y ” is ν_{Stark} and “ x ” is V^2 ; note this involves two separate determinations, one for $M = 0$ and one for $M = |1|$. For each case include a specific expression in the form of $\mu = f(m, \dots)$ where m is the slope of the linear fit.
- b)** Collect the experimental data required to determine the dipole moment. Submit a representative spectrum.
- c)** Prepare plots of ν_{Stark} vs. V^2 and calculate the value of μ for each trend. Note that the space between the Stark plate and the wall of the waveguide, d , is 4.64 mm for this instrument.

3.2. Visualizing a vibrationally-averaged bond length:

Sketch the potential energy curve for a diatomic molecule as a function of the bond length. Overlay a sketch of the potential energy curve for a harmonic oscillator with a similar force constant to the diatomic molecule. Explain the differences in the shapes of the curves between the two models. Add the vibrational energy levels to each curve. Note the position of the equilibrium bond length and the position of the average bond length for the ground vibrational state and excited vibrational states. Discuss the impact of the bond length on the rotational constant. If an isotopic substitution is performed on the diatomic molecule, what changes need to be made to the sketches?

3.3. Molecular vibrations:

In this activity you will calculate the values of α_1 , α_2 , and α_3 using the literature data and the method illustrated by Eq. 17. As a starting point, calculate the value for each α for $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ using the B_v value for the first vibrationally excited state of that mode. For example, $\alpha_1 = B_v(0,0,0) - B_v(1,0,0)$. Prove this method using Eq. 16. Use similar equations to calculate the values for α_2 and α_3 . Calculate the α coefficients for the ^{34}S and ^{13}C substituted molecular isotopes. Calculate a combined α correction to convert B_o to B_e for each isotope.

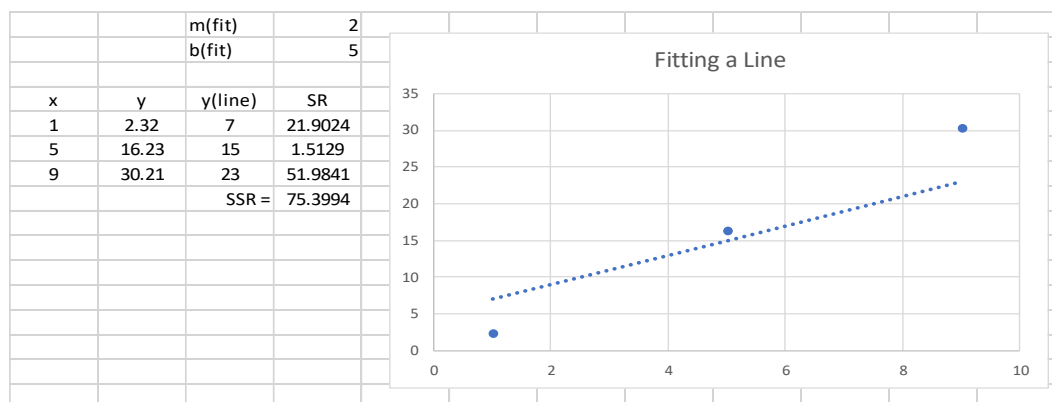
Day 4 Checklist

Preparation

- ☐ Watch the videos listed under the “Day 4 Videos” section on the course website.

Activities

- 4.1. *Conceptualizing a least squares fit:* Page 3 discusses using a least squares fit to determine the structure from an overdetermined set of data. As mentioned, there is one degree of freedom, which is similar to fitting a line to three data points. To help understand the process, you will set up a spreadsheet to do just that, but instead of using trendline or linest you will do the process manually. Start by replicating the spreadsheet, and plot, below. The points on the plot correspond to the x and y columns. The dotted line on the plot corresponds to the x and $y(\text{line})$ columns, where the $y(\text{line})$ column contains calculated values based on the slope and intercept given by $m(\text{fit})$ and $b(\text{fit})$. The SR column is the square of the residual, which is the square of the difference between y and $y(\text{line})$. The SSR cell is the sum of the square of the residuals, which is the sum of the SR values.



Once your spreadsheet is set up properly, play around with the $m(\text{fit})$ and $b(\text{fit})$ values to try to find the best fit line to the data. Start by just looking at the plot qualitatively as you modify the values. Then start looking at the SSR value and you should see a correlation that lower SSR values correspond to a better fit. Although it's easy to get a feel for the process, finding the best set of values is a bit challenging due to the correlation between slope and intercept. So as a final exercise, use Solver to minimize the SSR by modifying the slope and intercept (uncheck the “Make unconstrained variables non-negative” box when you do this). Verify the answer makes sense. In a real experiment it's important to note that the SR values should be reflective of the square of the noise in the experiment. Values particularly larger than that could indicate the data are nonlinear, or that there are problems in the measurements.

- 4.2. *Experimental measurements:* Measure the frequency of the unshifted peak of the $J = 1 \rightarrow 2$ transition for each molecular isotope. Make sure to choose appropriate values for all the input parameters when acquiring data. Submit the spectrum used to make the measurement for each isotope.
- 4.3. *Structure calculation:* Develop a spreadsheet similar to the example given on page 3 to determine the bond lengths from the experimental measurements made in the previous activity. Like the process for fitting a line in the previous activity, set up two cells for the two bond lengths, r_{CO} and r_{CS} . The calculations follow the logic given below:

$$r_{CO}, r_{CS} \rightarrow z_i \text{ (Eq. 1-3)} \rightarrow I \text{ (Eq. 4)} \rightarrow B_{fit} \text{ (Eq. 11)}$$

From the experimental data the logical flow is:

$$\nu \rightarrow B_o \rightarrow B_e \text{ (Eq. 16)}$$

This process is done for all three isotopes, so there are three B_{fit} values that are compared to the corresponding experimental values (Eq. 22). Solver is used to find the set of bond lengths that provide the best match between the experimental and calculated B values. Verify the functionality of your spreadsheet with a staff member.

Oral Exam Checklist

1. Sketch the energy levels of a rigid rotor for $J = 0$ through $J = 2$. Sketch the spherical harmonic wavefunctions for each state. Explain how the wavefunctions relate to the classical rigid rotor model.
2. Give the selection rules in the experiment and add the allowed transitions to the sketch of the energy levels. Provide a physical description for each selection rule. Explain how the selection rules would change if the microwave radiation was unpolarized instead of polarized.
3. Explain the Stark effect and modify the sketch of the energy levels to demonstrate the changes. Provide a physical description for the changes.
4. Sketch a spectrum for $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$, with a sweep range large enough to encompass the transition with and without the Stark field applied. Explain the features shown in the sketch.
5. What is the rotational constant and how does it relate to the moment of inertia? Explain why the moment of inertia is different for each molecular isotope analyzed in the experiment. Explain why the equilibrium bond length for r_{CO} and r_{CS} should not vary between the molecular isotopes.
6. Explain the difference between B_o and B_e in physical terms. Explain the α coefficients and provide a physical explanation for the sign of the α value associated with each normal mode.
7. Explain how the bond lengths are calculated from the experimental measurements of the three molecular isotopes. Explain why a unique pair of bond lengths cannot be determined from measurements of a single molecular isotope.
8. Explain how the dipole moment is calculated from the experimental measurements.
9. Explain how lock-in detection works and how it is implemented in this experiment.
10. Discuss your results. Explain the logic behind your choices of parameters for the spectra you chose to analyze.