

Course Module: Rotational Raman Spectroscopy

Course content

The learning goals of this lab course are to:

- (1) Understand fundamental concepts of spectroscopy.
- (2) Relate spectroscopic measurement results to physical properties.
- (3) Analyze a molecular structure based on spectroscopic data.
- (4) Learn to write a scientific report.

Introduction: Why we should learn about Spectroscopic measurements

Spectroscopy extends our senses into the world of atoms and molecules: We can observe and understand properties of atoms and molecules. Because all matter consists of atomic building blocks, this forms the basis of our understanding in all molecular sciences, from atomic physics to molecular biology. Unfortunately, spectroscopy cannot be understood without knowledge about quantum physics. Fortunately, there is no mysterious ‘magic’ involved in quantum physics and all required concepts can be boiled down to simple mathematical concepts and equations. In this guide, you will find all required concepts and equations to interpret rotational Raman spectroscopy and to connect spectroscopic results with molecular structure.

Rotational Raman spectroscopy is a subset of the methods used in the Schultz laboratory: We develop a novel type of spectroscopy called Correlated Rotational Alignment Spectroscopy (CRASY). A single CRASY measurement allows to observe molecular composition (via mass spectra), nuclear structure (via rotational Raman spectra), electronic structure (via electron spectra), and more. With CRASY, we try to remove a blind spot in the field of molecular spectroscopy: the spectroscopic characterization of impure (heterogeneous) molecular samples. Most samples we encounter are heterogeneous and chemists spend a lot of time and effort to purify their compounds of interest. In this module, we encounter isotopic heterogeneity: most atoms have naturally occurring isotopes and the spectroscopy of molecular isotopologues allows us to analyse molecular structure. If you are interested to learn more about the CRASY experiment, you can find explanations in an older lab-course guideline [here](#).

In the following, I give a simple introduction to some aspects of spectroscopy and the underlying quantum chemistry. You probably encountered most of the discussed topics in your lectures, possibly at much greater depth. But the goal of this course module is not to challenge you with deep theoretical insights, but instead to show you an example of modern spectroscopic measurements and to demystify the measurement and analysis of spectroscopic data.

Raman Spectroscopy

When electromagnetic radiation (light) interacts with matter, it may be absorbed, reflected, or scattered. Raman spectroscopy is based on the inelastic scattering of light in molecules (see Fig. 1). In a scattering process, light photons change their direction and can gain or lose some energy to their scattering partner, e.g., a molecule. This is different from absorption, where the complete photon energy is absorbed. Because molecules can only absorb or emit discrete (quantized) amounts of energy, the scattered *Raman light* can be used to identify and characterize molecular samples. The Raman

effect was first described by the Indian physicist Chandrasekhara Venkata Raman in 1928.

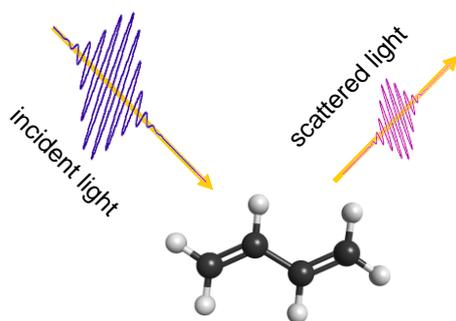


Fig 1: Inelastic scattering: The incident and scattered photons have different momenta and energy.

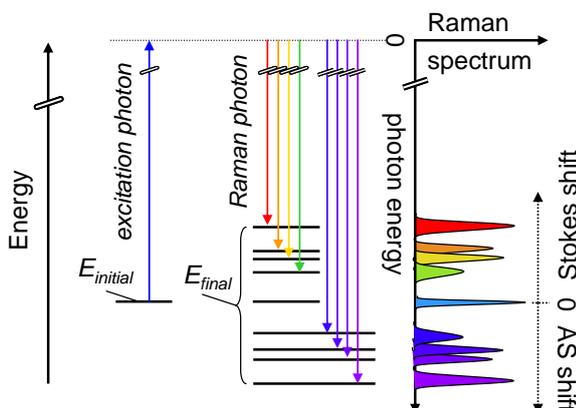


Fig 2: Energy scheme for Raman spectroscopy. An excitation photon (blue) is scattered and produces Stokes photons of lower energy (green-red) or anti-Stokes photons of higher energy (blue-purple).

The shift between the incoming and outgoing photon energy is called the *Raman shift*. The Raman process may deposit energy in the molecule (Stokes transition, cf. Fig. 2) or remove energy from the molecule (anti-Stokes transition). A common experiment is vibrational Raman spectroscopy: A powerful laser shines light with a single monochromatic wavelength λ onto a sample (corresponding photon energy $E_{in}=h\cdot c/\lambda_{in}$ with Planck constant h and speed of light c) onto a sample and a spectrometer analyses the wavelength λ_{out} of scattered photons. The measured energy difference $\Delta E = hc \cdot (1/\lambda_{in} - 1/\lambda_{out})$ corresponds to the energy absorbed or emitted by exciting one vibrational motion in the molecule. You can read more about vibrational Raman spectroscopy and how to set up a simple experiment with a laser pointer in one of our older [lab course guidelines](#).

Rotational Energy Levels

The energy levels of molecules are described within the framework of quantum physics: The molecule is described by a wave function $\psi_{molecule}$ that contains all relevant information about the potential and kinetic energy of each electron and nucleus in the molecule. We can use the tools of ab initio theory, e.g., the commercial software package [Gaussian](#) or the freely available [Orca](#), to calculate such wave functions to good approximation. For each wave function, we can calculate the quantized molecular energy E_{mol} by solving the [Schrödinger equation](#) $\hat{H}_{mol}|\psi_{mol}\rangle = E_{mol}|\psi_{mol}\rangle$ with the molecular Hamiltonian operator \hat{H} . (The actual recipe for finding ‘legitimate’ molecular wave functions ψ is to formulate all relevant particle interactions in the Hamiltonian and then to search for ψ s that give mathematical solutions to the Schrödinger equation.) The Dirac bracket formulation with $|\rangle$ is an abbreviation that denotes an integral.

Because the wave function describes all particles and motions, it is quite complex. Fortunately, we can separate it into several parts that are much easier to handle. We typically separate the wave function into an electronic, vibrational, rotational, and spin function:

$$\psi_{molecule} = \psi_{el} \cdot \psi_{vib} \cdot \psi_{rot} \cdot \psi_{spin} \quad \rightarrow \quad E_{mol} = E_{el} + E_{vib} + E_{rot} + E_{spin} \quad (\text{eq.1})$$

We can therefore interpret spectroscopic results tied to a change in a particular molecular motion (e.g., rotation) by considering a much simpler mathematical description (e.g.: $\hat{H}_{\text{rot}}|\psi_{\text{rot}}\rangle = E_{\text{rot}}|\psi_{\text{rot}}\rangle$). The [rotational Hamiltonian operator](#) \hat{H}_{rot} is tied to the angular momentum and we can find a general solution for rotational energies, as a function of the molecular inertial moment I_{mol} , the Planck constant \hbar , and a quantum number J :

$$\hat{H}_{\text{mol}}|\psi_{\text{mol}}\rangle = E_{\text{mol}}|\psi_{\text{mol}}\rangle \quad \rightarrow \quad E_J = J \cdot (J+1) \cdot \hbar^2 / (2 \cdot I_{\text{mol}}), \quad J = 0, 1, 2, \dots \quad (\text{eq. 2})$$

The energy term $\hbar^2 / (2 \cdot I_{\text{mol}})$ is often expressed as rotational constant B in units of frequency ($B = E/h$) or wavenumbers ($B = E/hc$). Here I will use B in units of frequency, with the relation :

$$I = \hbar / (4\pi \cdot B) \quad (\text{eq. 3})$$

Non-linear molecules can perform complex rotations around more than one axis and a complete description then involves additional quantum numbers and energy terms. In this case, we obtain up to three distinct rotational constants A , B , and C , which describe the rotation around three spatial axes a,b,c. Feel free to learn more about the solutions to the rotational Schrödinger equation, e.g., with the excellent chapters in the [LibreText Chemistry textbook](#). Here we will ignore this additional complexity and only consider one-dimensional rotation.

The molecular inertial moment I is described by the mass m_i and position r_i of the atoms in the molecule. We can therefore directly connect experimentally determined rotational energies E_J to atomic positions r_i within the molecular frame (substitute eq. 4 in eq. 2 and solve for r_i):

$$I = \sum_{i=1}^n m_i \cdot r_i^2 \quad (\text{eq. 4})$$

Spectroscopic Selection Rules

We cannot directly observe the energy of a molecule, but we can observe the interaction of the molecule with other particles. The interaction with photons is particularly simple to understand: photons do not have rest mass and contain only an easily described

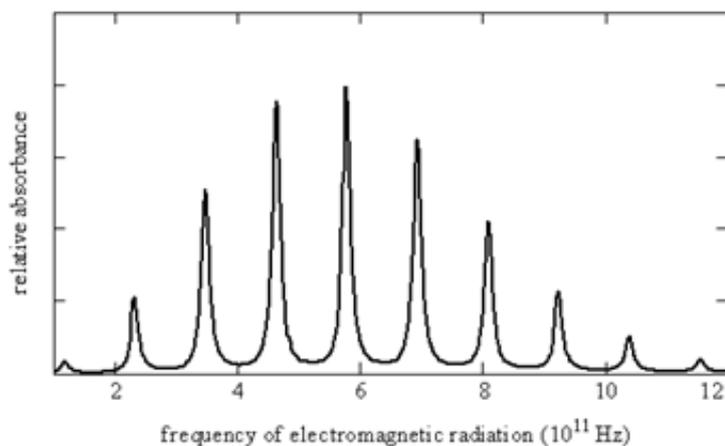


Fig. 3: The rotational spectrum of $^{12}\text{C}^{16}\text{O}$ at 40 K temperature. Figure reproduced from LibreText Chemistry textbook [bit.ly/3wfh0Hs].

quantized energy $E = h\nu$ and momentum $p = h\nu/c$ with photon frequency ν , light speed c , and Planck's constant h . Photon absorption (or emission) means that the full photon energy and impulse were transferred from the photon into the molecule (or from the molecule into a photon). By characterizing the energy E_{ph} of an absorbed photon, we learn about the energy difference $E_{\text{ph}} = \Delta E_{\text{initial} \rightarrow \text{final}} = E_{J,\text{final}} - E_{J,\text{initial}}$ between two energy levels in the molecule.

Fig. 3 shows the rotational spectrum of carbon monoxide. To relate the position of absorption lines in the spectrum to state energies E_J and structural parameters r_i , we need to first determine the state quantum numbers J_{initial} and J_{final} for the molecular state before and after photon absorption. Photon absorption is only allowed for particular combinations of initial and final states, which are described by spectroscopic 'selection rules'. To understand the selection rules, we must consider the interaction between the photon electric field and the molecule. The strongest interaction is between the light electric field and the molecular dipole μ : The light electric field will pull the molecule to align the molecular dipole in the field as illustrated in Fig. 4.

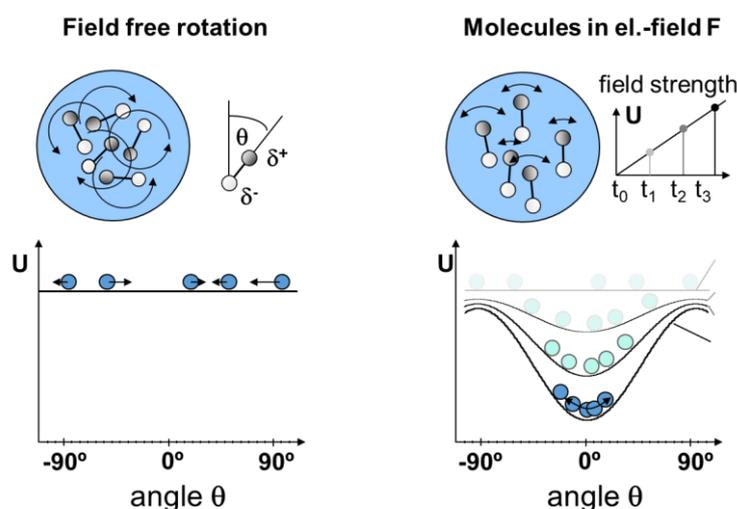


Fig. 4: Molecular motion in an electric potential U . (Left) Without electric field, the molecular energy is independent of the spatial orientation and molecules rotate freely. (Right) In an electric field U , the energy of the molecule depends on the angle θ between the molecular axis and the electric field axis. Molecules feel an angular force and may be pulled into 'alignment' (angular orientation).

In quantum physics, the photon-molecule interaction can be modeled by perturbation theory. We obtain equations that describe the probability for photon absorption as function of the initial and final wave functions ψ_{initial} , ψ_{final} and a transition dipole μ_T :

$$P_{\text{absorption}} = \langle \psi_{\text{final}} | \mu_T | \psi_{\text{initial}} \rangle \quad (\text{eq. 5})$$

The transition dipole for rotational spectroscopy is simply the molecular dipole. Solving the corresponding absorption probability equation $P_{\text{rot}} = \langle \psi_{\text{rot}, J_{\text{final}}} | \mu | \psi_{\text{rot}, J_{\text{initial}}} \rangle$ shows that only transitions with $\Delta J = J_{\text{final}} - J_{\text{initial}} = \pm 1$ are allowed. We can now calculate expected transition energies (I substitute the frequency $\nu = E/h$ and rotational constant $B = \hbar^2/(4\pi \cdot I_{\text{mol}})$ in the second line):

$$\begin{aligned} \Delta E &= E_{\text{final}} - E_{\text{initial}} = \hbar^2/(2 \cdot I_{\text{mol}}) [J_{\text{final}} \cdot (J_{\text{final}} + 1) - J_{\text{initial}} \cdot (J_{\text{initial}} + 1)] \\ \Delta \nu &= B [(J_i + 1) \cdot (J_i + 2) - J_i \cdot (J_i + 1)] = 2B \cdot (J_i + 1), \quad J_i = 0, 1, 2, \dots \end{aligned} \quad (\text{eq. 6})$$

If a molecule has no dipole, then we cannot observe rotational spectra: the value for μ_T in eq. 5 is zero. The transition dipoles for Raman scattering are dipoles μ_{ind} induced by the light electric field F : The electric field pulls on nuclei and electrons creating a dipole

$\mu_{\text{ind}} = F \cdot \alpha$ even if the molecule does not have an inherent dipole. The induced dipole is proportional to the molecular polarizability α . Solving eq. 5 for the Raman transition moment leads to different selection rules and allowed transitions $\Delta J = J_{\text{final}} - J_{\text{initial}} = \pm 2$.

You can read more about selection rules in the corresponding [Libre Text chapter](#). But be aware that the a priori derivation of selection rules requires an understanding of perturbation theory and is not typically covered in chemistry textbooks.

Calculating a Diatomic Bond Length from Rotational Data

We can now analyze the spectrum in Fig. 3. Note that CO has a dipole and the spectrum is not a Raman spectrum, i.e., the selection rules are $\Delta J = \pm 1$. The observed absorption line positions are (in MHz): 115271, 230538, 345796, 461041, 576268, 691473, 806652, 921780, 1036912, 1151985 [see: [LibreText Chemistry](#)]. If I assume that the first line corresponds to $J_i = 0$, I obtain $2B = 115271$ MHz; $B = 57635.5 \cdot 10^6$ Hz and can calculate the CO inertial moment:

$$I_{\text{CO}} = \hbar / (4\pi \cdot B) = 1.45604981 \cdot 10^{-46} \text{ kg} \cdot \text{m}^2.$$

We could take any other line and guess the J_{initial} quantum number; if guessed correctly, we will get the same value for B . If it is difficult to guess the J_{initial} quantum number, it is possible to just look at the energy difference $\Delta \Delta v$ between any two adjacent lines to obtain B :

$$\Delta \Delta v = \Delta v_{n+1} - \Delta v_n = 2B \cdot (J_i + 2) - 2B \cdot (J_i + 1) = 2B$$

With eq. 4, we can calculate a bond length for the molecule based on B , but we need to substitute the positions r_C, r_O of the atoms with a bond length $r_{\text{CO}} = r_C + r_O$. This can be done by determining the molecular center-of-mass, which allows us to substitute $r_C = r_{\text{CO}} \cdot m_O / (m_C + m_O)$, $r_O = r_{\text{CO}} \cdot m_C / (m_C + m_O)$ (see: [Wikipedia](#)) and to formulate:

$$I_{\text{CO}} = \mu \cdot r_{\text{CO}}^2, \quad \text{with reduced mass } \mu_{\text{CO}} = m_C \cdot m_O / (m_C + m_O) \quad (\text{eq. 7})$$

With the atomic masses $m(^{12}\text{C}) = 12$ amu, $m(^{16}\text{O}) = 15.995$ amu and the [atomic mass unit](#) amu = $1.66054 \cdot 10^{-27}$ kg, we can solve for the bond length:

$$r_{\text{CO}} = \sqrt{I_{\text{CO}} / \mu_{\text{CO}}} = 1.1309 \cdot 10^{-10} \text{ m},$$

The result is quite close to the [value given by the US standards body NIST](#). Note that instead of the step-wise analysis, I could just write the full equation relating the bond length to the measured rotational constant:

$$r_{\text{CO}} = \sqrt{I_{\text{CO}} / \mu} = \sqrt{\frac{\hbar}{4 \cdot \pi \cdot B} \cdot \frac{m_C + m_O}{m_C \cdot m_O}} \quad (\text{eq. 8})$$

Calculating Bond Lengths from Isotopologue Data

In the example of CO, above, we could write down one equation (eq. 8) relating the bond length to the measured rotational constant. If there is more than one bond parameter, one equation will not be sufficient to determine multiple bond lengths and / or bond angles. With the analysis of isotopologues, i.e., molecules where one atom is replaced by an isotope of different mass, we can resolve this problem. For each isotopologue we can measure one rotational constant B (or three constants A, B, C in the case of nonlinear molecules) and write a corresponding equation (based on eqs. 3 and 4)

to relate the isotope position r_i to the measured constant. If two isotopologues differ by only one atomic isotope, we obtain the equation:

$$I_{iso1} - I_{iso2} = \frac{\hbar}{4\pi B_{iso1}} - \frac{\hbar}{4\pi B_{iso2}} = m_{0,iso1}r_0^2 + \sum_{i=1}^n m_i r_i^2 - (m_{0,iso2}r_0^2 + \sum_{i=1}^n m_i r_i^2) = (m_{0,iso1} - m_{0,iso2})r_0^2$$

↑ *unchanged atoms*
↑ *changed atom*

(eq. 9)

This equation assumes that the molecular center-of-mass remains unchanged because otherwise the inertial moment contributions for the unchanged atoms are not identical. It is not mathematically difficult to account for a changed center-of-mass, but the equations become cumbersome and the analysis is best performed by computer algorithms. General equations suitable for such isotopologue structure analysis were described in 1953 by Kraitchman [1] and advanced methods were summarized by Watson in 1999 [2].

Your Assignment

It is your assignment to try and analyze the molecular structure of one molecule based on data measured in our CRASY laboratory. Below you find tables of rotational constants for carbon disulfide (CS_2) and benzene. Neither molecule is a linear diatomic, but CS_2 is a linear molecule with only one bond length (r_{CS}) and benzene is highly symmetric and has only two bond lengths (r_{CC} and r_{CH}). In both cases, you can identify symmetric isotopologues, where the center-of-mass remains unchanged and where you can use eq. 9 to calculate the center-of-mass distances r_i for each atom.

If you are unsure how to proceed, please ask me (schultz@unist.ac.kr) or my PhD student Begum Rukye Ozer (begumrukiyeozer@gmail.com) after you read and understood the basic concepts described in this guideline. On your Lab Course Day (week of Nov. 16), we will have a Zoom meeting where you can ask questions and present your progress to get feedback.

Rotational Constants for Benzene and Carbon Disulfide Isotopologues

Benzene is a D_{6h} symmetric molecule and is depicted in Fig. 5. Rotational constants are given in Table 1. For details on the measurement of benzene rotational constants by CRASY, see reference [3]. For symmetric isotopologues, the inertial moment is given by the following equation:

$$I = \sum_{i=1}^n m_i \cdot r_i^2 = 6 \cdot m_C r_C^2 + 6 \cdot m_H r_H^2$$

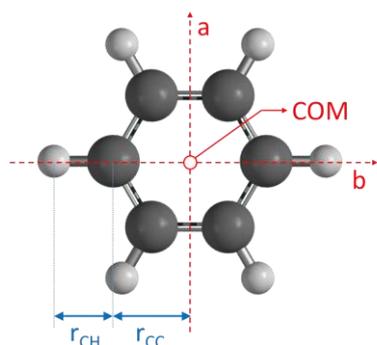


Fig. 5: Benzene geometry. Note that the distance r_C of carbon atoms to the center-of-mass (COM) is identical to the r_{CC} bond length and the COM distance for hydrogen atoms is $r_H = r_{\text{CC}} + r_{\text{CH}}$. Due to symmetry, the rotational constants A and B for rotation around axes a and b are identical and the rotational constant C for rotation around axis c (out-of-plane) is $C = A/2 = B/2$. If isotopic substitution breaks the symmetry, independent $A, B,$ and C constants can be determined.

Table 1: Benzene isotopologue rotational constants determined by a CRASY experiment. Rotational constants A, B, and C were fitted to the stated number of observed rotational Raman transition Lines in a mass-selected spectrum. Numbers in brackets give the 1- σ standard uncertainty in the corresponding last digits.

Isotopologue	Mass (u)	A (MHz)	B (MHz)	C (MHz)	Lines	Distortion constants omitted
C ₆ H ₆	78		5689.3129(48)		16	
¹³ C-C ₅ H ₆	79	5689.460(18)	5568.429(18)	2822.9(28)	27	
¹³ C ₆ H ₆	79		5338.116(93)		18	
C ₆ D ₆	84		4707.3193(29)		17	
¹³ C-C ₅ D ₆	85	4707.472(24)	4624.237(23)	2329.1(46)	21	

Carbon disulfide is a linear triatomic molecule as depicted in Fig. 6. Measured rotational constants are given in Table 2. For details on the measurement of CS₂ rotational constants by CRASY, see reference [4]. For symmetric isotopologues, the carbon atom is at the center-of-mass ($r_C=0$) and does not contribute to the inertial moment:

$$I = m_C \cdot r_C^2 + 2 \cdot m_S \cdot r_S^2 = 2 \cdot m_S \cdot r_S^2$$

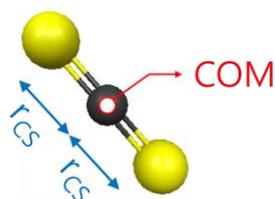


Fig. 6: Carbon disulfide geometry. The carbon atom is at the center-of-mass (COM) and the linear molecule is completely described by the r_{CS} bond length.

Table 2: CS₂ isotopologue rotational constants determined by a CRASY experiment. The state Σ_g corresponds to the vibrational ground states, state Π_u is a vibrationally excited state with an excitation of the S-C-S molecular bending mode. Numbers in brackets give the 1- σ standard uncertainty in the corresponding last digits.

Isotopologue	Mass	State	Rotational constant B_{eff}^*			Centrifugal distortion D_{eff}		
			This work	Literature	Ref.	This work	Literature	Ref.
³² S ¹² C ³² S	76	Σ_g	3,271,517.0 (0.7)	3,271,516.5 (1.5)	20	355 (3)	352.79 (9)	20
	76	Π_u^e	3,276,738 (9)	3,276,759 (12)	18	347 (58)	359.1 (6)	18
	76	Π_u^f	3,279,064 (7)	3,279,077 (11)	18	386 (38)	360.6 (6)	18
³² S ¹³ C ³² S	77	Σ_g	3,271,634.6 (1.3)	3,271,637.8 (0.3)	21	346 (7)	350.76 (2)	21
³² S ¹² C ³³ S	77	Σ_g	3,221,849.4 (2.6)	3,221,843 (11)	18	329 (13)	341.3 (1.1)	18
³² S ¹² C ³⁴ S	78	Σ_g	3,175,020.4 (1.2)	3,175,024 (8)	18	318 (6)	332.6 (5)	18
³² S ¹³ C ³⁴ S	79	Σ_g	3,175,120 (18)	3,175,115.1 (1.3)	21	318 (95)	332.94 (15)	21
³⁴ S ¹² C ³⁴ S	80	Σ_g	3,079,422 (9)	3,079,377 (27)	18	339 (48)	346 (16)	22

The most precise literature values are given for comparison. Values in parentheses denote the 1 σ standard deviation for the corresponding last digits.

*For the vibrationally excited Π_u states, B_{eff} differs from B due to the l-type splitting.

Report

Your report should be based on the American Chemical Society (ACS) [manuscript template](#). Please change the line spacing to **double-spaced** so I can correct your report and give you feedback. I uploaded further information and an English Writing Style Guide on our [CRASY website](#). Please take some time to write a good report; otherwise I

will demand a revised and corrected report from you. The report should be 2 to 4 pages long and contain Equations, Figures, and Tables as required to explain and illustrate the contents.

For your report, please write a one-paragraph *Introduction* summarizing your understanding of rotational spectroscopy and molecular structure analysis. Feel free to cite literature that helped you understand the topic in this section. Then describe your analysis in a *Results* section. Describe each step you took to choose the relevant data and analyze it. Describe it in a manner that the reader can reproduce every step and arrive at the same result. Write a *Discussion* section and discuss how trustworthy, precise, and accurate your results are. Can you explain what might limit the accuracy of your result? Find relevant literature, e.g., crystal structures for benzene [5] and CS₂ [6] and compare your results to literature. Can you find advantages or disadvantages of your analysis as compared to literature data?

Literature

- [1] [J. Kraitchman, American Journal of Physics 21, 17–24 \(1953\).](#)
- [2] [J. K. Watson, A. Roytburg and W. Ulrich, J. Mol. Spectr. 196, 102–119 \(1999\).](#)
- [3] [J.C. Lee, D.E. Lee and T. Schultz, Phys.Chem.Chem.Phys. 21, 2857 \(2019\).](#)
- [4] [C. Schröter, J. C. Lee and T. Schultz, PNAS 115, 5072–5076 \(2018\).](#)
- [5] [E.G. Cox and J.A.S. Smith, Nature 173, 75 \(1954\).](#)
- [6] [N.C. Baenziger and W.L. Duax J. Chem. Phys. 48, 2974 \(1968\).](#)