Questions on this cume are drawn from the attached article, entitled

*Measurement of Sulfur Isotope Compositions by Tunable Laser Spectroscopy of SO₂*

Where specific passages are relevant, they have been marked in the paper with the corresponding question number. The questions are marked with point values, partly to provide an indication of the relative emphasis and expected level of detail. Keep your answers succinct and on-topic; points will be deducted for irrelevance. Many of these questions can be fully answered in 2-3 short sentences. Write clearly – what cannot be read cannot be graded.

**Question 1 (10 points):** Conclude the goal of this project.

To develop and to demonstrate the feasibility of a measurement technique for analyzing SO₂ isotope ratios. Measuring these ratios from solids reveals the samples (rocks) formation process or their past in general.

**Question 2 (5 points):** Explain in your own words what $\delta^{34}$S measures. (short answer)

It measures the SO₂ isotope ratio of a sample relative to that of a reference sample. Thus, it can be positive or negative number; the latter one is found when the sample has a lower isotope ratio than the reference.

**Question 3 (5 points):** What type of absorbances (Fig. 2 bottom) is analyzed? Or in other words, what type of molecule excitation is utilized? (short answer)

Rotational excitations of SO₂ as part of a vibrational excitation

**Question 4 (5 points):** Why is laser spectroscopy as opposed to FTIR an appropriate measurement technique for this project?

Only laser spectroscopy can achieve high enough wavelength resolution. From Fig. 2 we see that a resolution of <0.01cm⁻¹ is required. With FTIR a typical resolution is 1-4cm⁻¹ or when pushing it 0.1cm⁻¹. FTIR would not be able to resolve the rotational excitations which are different for different isotopes.

**Question 5 (5 points):** What is the main advantage of laser spectroscopy over ‘isotope ratio mass spectrometry’? (short answer)

Laser spectroscopy can easily discriminate between $^{34}$S$^{16}$O₂ and $^{32}$S$^{18}$O$^{16}$O – it requires “corrections” in IRMS since both molecules have the same nominal mass.

**Question 6 (15 points):** In the right column of p. 9263 the ‘laser current’ is discussed. Explain what components it contains and what impact on the laser emission wavelength it has and what signals are generated. A drawing might help.
A ramp scans the laser’s emission frequency (i.e. over wavenumber); at the end of a ramp, the current drops back = emission frequency jumps back and the laser is scanned over the frequency range again. The 20 kHz modulation (small amplitude) makes the emission frequency wiggle back and forth on top of the ramp. This introduces AC signal components that are proportional to the absorption spectrum’s derivatives with respect to wavelength. (more: Skoog 5th ed. chapter 14D-3). The paper calls the second derivative the “second-order Fourier component”.

**Question 7 (10 points):** What is the purpose of wavelength modulation. Hint 1: Under which other name is ‘Wavelength Modulation Spectroscopy’ also known? Hint 2: Compare the WMS signal (Fig.2 – bottom) to the corresponding absorbance spectrum.

WMS is also known as derivative spectroscopy since the wavelength modulation generates the absorbance spectrum’s 1st derivative as the amplitude of an AC signal component at modulation frequency, 2nd derivative as the amplitude of an AC signal component at 2 x modulation frequency (used here) and so on.

**Question 8 (10 points):** It is stated that the wavelength modulation signal achieves “significantly better signal-to-noise ratio than direct absorption spectroscopy”. Explain why? Hint: By means of what electronic equipment is such a signal (Fig. 2 bottom) measured?

Derivative signals are measured by means of lock-in amplifiers tuned to the modulation frequencies or here 2 x modulation frequency (2nd derivative). Lock-ins are rather insensitive to long-term signal drifts and only “capture” the noise with frequencies that fall inside its very narrow frequency bandwidth.
Question 9 (20 points): Deriving equ (7) is not very clear. Discuss how this equation is derived (use equ (2) – (7)) and clearly state which measurement signals are utilized to determine $^{34}\text{S}/^{32}\text{S} = [^{34}\text{SO}_2]/[^{32}\text{SO}_2]$.

Hint: $\ln(1 - \alpha_x) = -\sum_{n=1}^{\infty} \frac{\alpha_x^n}{n} = -\alpha_x \sum_{n=0}^{\infty} \frac{\alpha_x^n}{n+1}$ - note the difference in the sums: $n = 1$ and $n = 0$

We need $P_{o,x}$ which is the “power” (= intensity) at the wavelength position of the $^x\text{SO}_2$ line when the gas is not present (Fig. 2 middle).

$W_x$ is the difference of the 2nd derivative’s $^x\text{SO}_2$ peak (Fig. 2 bottom) and the minimum of the 2nd derivative of the Gaussian absorbance feature at the higher frequency (!).
(2): $X_x = 1 - \frac{P_x}{P_{0,x}} = 1 - \exp(-\sigma_x \cdot l \cdot [x])$

Beer's Law: $X = 32\cdot x$

$\Rightarrow \exp(-\sigma_x \cdot l \cdot [x]) = 1 - X_x$

$-\sigma_x \cdot l \cdot [x] = \ln(1 - X_x)$

$$\lim_{x \to \infty} \sum_{n=1}^{\infty} \frac{X_x}{\eta} = -X_x \sum_{n=0}^{\infty} \frac{X_x}{\eta x}$$

$\Rightarrow \frac{X_x}{\sigma_x \cdot l} = -X_x \phi_x$

$$\Rightarrow \frac{X_x}{\sigma_x \cdot l} = \frac{\phi_x}{\phi_x} = 1$$

(3) $\omega_x \cdot \Gamma_x = \chi \cdot P_{0,x} \cdot X_x$

$\Rightarrow \chi_x = \frac{\omega_x \Gamma_x}{\chi \cdot P_{0,x}}$

$\Rightarrow \frac{\chi_x}{\omega_x \cdot P_{0,x}} = \frac{\eta_x}{\sigma_x \cdot l}$

$\Rightarrow \frac{\chi_x}{\sigma_x \cdot l} = \left\{ \begin{array}{ll} 345 \sigma_x & \text{for } \chi_x > 0 \\ 32 \sigma_x & \text{for } \chi_x < 0 \end{array} \right.$
**Question 10 (15 points):** State what you think is the biggest challenge in the project – give reasons.

Isotopes have very similar spectroscopic properties but this can be handled by means of laser spectroscopy providing high enough wavelength resolution.

True, below equ (4) it is stated that modeling (not measuring!) pressure and temperature effects on $W_{34}/W_{32}$ were found to be negligible but in reality this is often not the case.

Main challenge: The isotope ratios are very small, i.e. one isotope is clearly dominating. On top of this, sample preparation and handling without changing the isotope ratio was shown to be very tricky and a major source of uncertainty.