Course Module: Correlated Rotational Alignment Spectroscopy

Course content

Do you remember those textbook problems where "laboratory A measured something but requires your help to analyze the data"? Well, this year we have a problem like this from our own lab: We measured mass-correlated rotational Raman spectra and the calibration of our rotational spectra drifted away from the properly calibrated 'true' value. It is now your job to analyze some of our old spectra to track down the size of the calibration error over time.

The learning goals of this lab course are to:

(1) Understand correlated and Fourier-transform spectroscopy.
(2) Learn to analyze rotational Raman spectra of linear molecules.
(3) Learn to write a scientific report.

Your specific tasks are:

Preparation	(1) Download and install the CRASY data analysis software.
	(2) Download and analyse at least 5 CRASY data-sets.
Interactive	(3) Participate in the Lab-course session, discuss your results, review your colleagues' results, analyse 5 more data-sets.
Report	(4) Submit a report summarizing your results.

Introduction of the CRASY measurements

In the Schultz laboratory, we develop a novel type of spectroscopy called Correlated Rotational Alignment Spectroscopy (CRASY). A single CRASY measurement allows to assign multiple molecular properties, such as molecular composition (via mass spectra), nuclear structure (via rotational spectra), electronic structure (via electron spectra), and more. The data you will see comes from mass-CRASY measurements, combining information from mass and rotational Raman spectra in a two-dimensional data set.

Why do we develop a new type of spectroscopy? Modern scientific and technological progress is based on the observation of the natural world, its description with qualitative or quantitative models and, finally, the utilization of our model-based understanding for theoretical or practical advances. All your University courses teach you such model-based understanding. We can only model and understand those things we can observe. The absence of technologies to observe certain types of matter or interactions leaves us with blind spots. We cannot even assess how many things we miss if we cannot see them! With CRASY, we try to remove a blind spot in the field of molecular spectroscopy: the spectroscopic characterization of impure (heterogeneous) molecular samples.

Most molecular samples are inherently heterogeneous and chemists routinely purify their compounds of interest, e.g., from a natural sample or a synthetic mixture. Purification is time consuming, difficult, and in some cases outright impossible (e.g., for molecular tautomers or instable species). Spectra for heterogeneous samples show averaged spectroscopic signals that are often insufficient to identify properties of individual sample components. Would it not be nice if we could mark each sample

component and subsequently sort our spectroscopic results to separate the signals for each component?

In CRASY measurements, molecules in the sample are 'marked' by correlation to a high-resolution rotational Raman spectrum. You can think about the rotational spectrum as a unique molecular fingerprint that is attached to all other spectroscopic data. This fingerprint allows us to separate the signals from different molecules and to assign each signal to a particular molecular species. Even better, the rotational spectrum tells us about the shape of the molecule and can be used to analyze molecular structure with extraordinary resolution.

These are still the early days of CRASY measurements (currently, our experiment is unique in the world). But on top of the correlation described above, rotational Raman spectra obtained by CRASY already reached orders-of-magnitude better resolution than data from any preceding experiment. Also, we learned to directly calibrate measured rotational frequencies against an external frequency standard (a clock), creating the first "absolute frequency" measurements of their type. However, somewhere in the years between 2017 and 2020, the CRASY calibration clock lost its lock against the GPS frequency standards (atomic clocks at NIST), leading to slowly increasing calibration errors.

As part of this lab course, it is your job to identify the calibration error in CRASY data-sets and to help us identify how the errors changed over time.

CRASY Measurement Technology

You probably already learned about multidimensional NMR spectroscopy: Richard Ernst won a Nobel prize in 1991 for the development of these techniques. For example, his COSY method used two radio-wave pulses to create a two-dimensional spectrum that allows to assign the bonding pattern even in extremely large molecules (see also: Nobel prize of Kurt Wüthrich in 2002). CRASY is inspired by this work, but uses laser pulses instead of radio-waves to create two-dimensional spectra in the optical regime. As in NMR, the experiment is performed in the time domain. But where NMR excites and probes the rotating magnetization vectors of nuclear spins, CRASY excites and probes the rotation of molecules.

Any excitation of a molecule is tied to the molecular excitation dipole (for one-photon excitation), or its polarizability (for two-photon, or Raman excitation). These excitation moments are tied to the molecular structure, as illustrated for a linear molecule in Fig. 1. A molecular excitation therefore leads to an orientational selection of the molecules, as shown in Fig. 2. If we excite rotational states, then the excited molecules will rotate faster (or slower) than the unexcited molecules. After a while, the faster rotating molecules catch up to the slower ones, leading to a net alignment of the molecules.

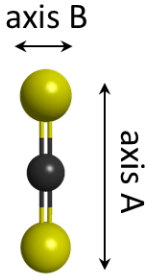

Fig. 1: Polarization anisotropy of a linear molecule (CS_2). Electrons can move an extended distance along the molecular bonds (axis A), but are very constraint in their motion perpendicular to the bonds (axis B). The molecular is therefore quite polarizable along axis A, but not axis B.
The transition moment for rotational Raman excitation is due to the polarizability anisotropy, i.e., the difference in polarizability along the molecular axes. We therefore expect large Raman transition moments for linear molecules such as CS_2.

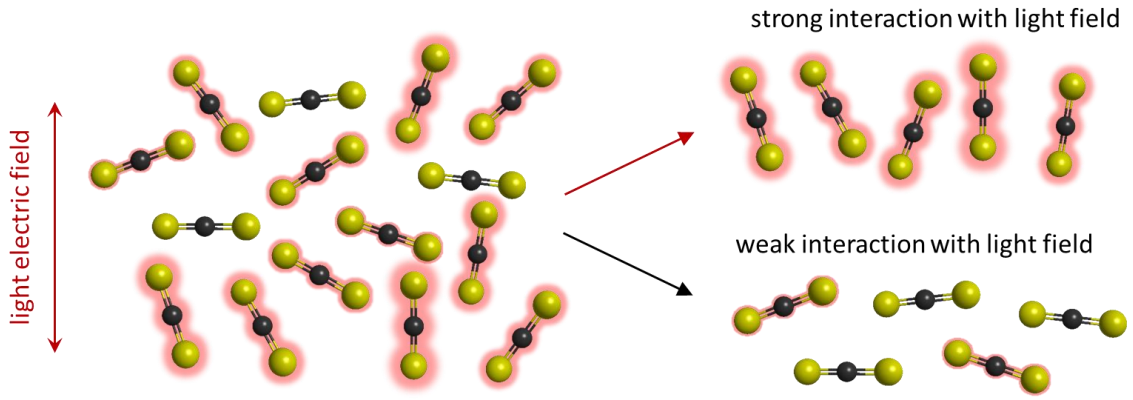

Fig. 2: Rotational Raman interaction of molecules with linearly polarized light (left). The light electric field interacts strongly with molecules whose most polarizable axis is parallel to the light electric field. Rotational Raman excitation therefore selectively excites molecules with particular molecular alignment (top right), but not others (bottom right).

In CRASY, we probe that alignment by a second optical excitation step. Many molecules will be excited in the moment when the molecular alignment orients the excitation dipoles parallel to the axis of the probing light field. We then observe a large signal. A moment later, the molecular rotations turn the excitation dipoles out of the probing laser field axis, reducing the amount of detectable signal. By observing the signal changes as function of time, we can measure the frequencies of molecular rotation.

Here is a link to a video illustrating how molecular rotation is observed in the time domain: https://blackboard.unist.ac.kr/bbcswebdav/pid-143761-dt-content-rid2816476_1/xid-2816476_1

In mass-CRASY, we first excite molecular rotations by rotational Raman excitation. We then observe the resulting rotational motion by two-photon ionization (electronic excitation, followed by photoionization) with detection of formed ion in a mass spectrometer. By detecting the mass spectra at different time delays between the rotational excitation and probing, we observe molecular rotation as signal modulations in each mass signal. Fig. 3 shows an example for such delay-dependent mass spectra.

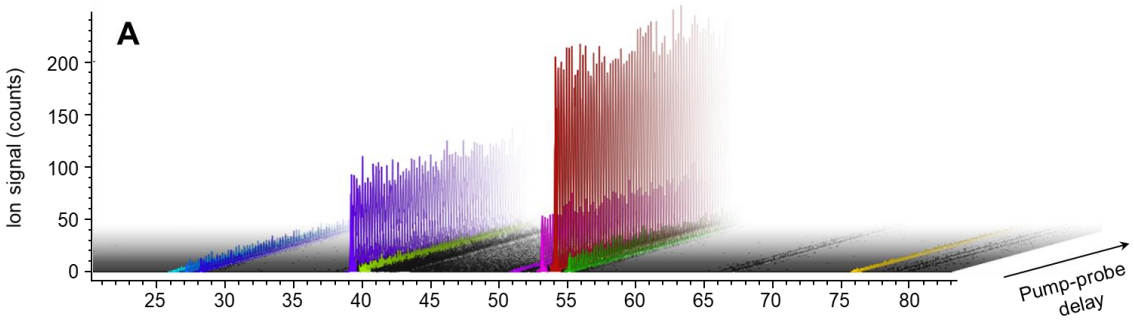

Fig. 3: Sequence of mass spectra measured for a sample of 1,3-butadiene at different pump-probe delays. Ion signals are observed for butadiene (mass 54 u, red), its fragments (<54 u, colors pink–purple–blue–turquoise), its heavy isotopologue (55 u, color green), and CS_2 (76 u, color yellow). Each ion signal shows delay-dependent amplitude modulation due to molecular rotation.

To obtain information about the rotational motion of the molecule, we can select one mass signal and plot the signal amplitude as function of the time delay. Note that different ion signals stem from different molecules and therefore show different

frequencies for their signal modulation. We now inherently tied the information about rotational motion to that of molecular mass. Fig. 4 (left) shows the time-dependent signals for several CS_2 isotopologues [see: Science **333**, 1011 (2011).]. Note how moments of maximum alignment leads to periodic signal maxima and minima.

To analyze molecular properties, we really want a "spectrum" of transition frequencies, not a time-dependent trace. We obtain this spectrum by Fourier transformation of the time-dependent trace. If you have not yet learned about Fourier transformation, I suggest you watch an excellent introductory video at [https://youtu.be/spUNpyF58BY]. Fig. 4 (Right) shows the rotational Raman spectra for the time dependent traces in Fig. 4 (Left).

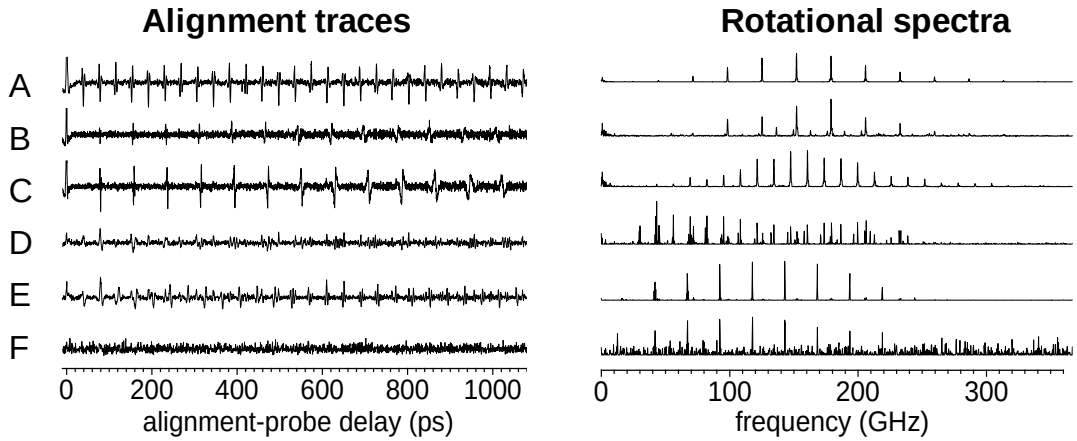

Fig. 4: (Left) Alignment traces, i.e., delay dependent ion signals, for carbon disulfide isotopologues at mass 76 u to 81 u (A to F). (Right) Rotational spectra obtained by Fourier analysis of traces A to F.

The spectroscopic resolution for the rotational Raman spectrum is expected to be proportional to the observation period (the range of the delay axis). Heisenberg's uncertainty relation predicts a resolution limit of $\sigma(energy) \cdot \sigma(time) \geq \hbar/2$. This roughly translates into an expected frequency resolution (width of each frequency peak) of $\Delta\nu = 1/(t_{max} - t_{min})$, with the delay values t_{min} for the first and t_{max} for the last delay.

Analysis of Rotational Raman Spectra

The rotational energy of a molecule corresponds to the kinetic energy of its rotating atoms (we sum over atoms *1…n*):

$$T = \sum_n \frac{1}{2} m_n v_n^2 .$$

Each atom travels on a circular orbit with length $l_n = 2\pi r_n$ around the molecular center-of-mass. The velocity v_n is therefore easily expressed as function of the angular rotational frequency ω ($\omega = 2\pi\nu_{rot}$) as $v_n = r_n\omega$. We can therefore express the kinetic energy as:

$$T = \sum_n \frac{1}{2} m_n l_n^2 \omega^2 .$$

We can remove all atom-dependent variables with the definition of the molecular angular momentum:

$$L = \sum_n m_n l_n^2 \omega .$$

Expressing the kinetic energy as function of the molecular angular momentum L allows us to move from classical equations to quantum mechanical equations by substituting the angular momentum with the quantum mechanical angular momentum operator:

$$T = \frac{L^2}{2I} \qquad \hat{T} = \frac{\hat{L}^2}{2I} \qquad \hat{H} = \hat{T} = \frac{-\hbar^2}{2\mu}\nabla^2$$

(classical) → (classical / quantum) → (quantum)

(μ represents the reduced mass of the complete molecule with $I = \mu l^2$.) For a rigid linear molecule (e.g., CS_2), solutions to the quantum mechanical Schrödinger equation $E\psi = H\psi$ give quantized solutions as function of the rotational quantum number J:

$$E = \frac{\hbar^2}{2I} J(J+1), \qquad J = 0,1,2,\ldots$$

The centripetal force in a rotating molecule will stretch the molecular bonds, thereby increasing the inertial moment of the molecule. If we assume a harmonic bonding potential with vibrational wavenumber ω_e, this adds a second term to the rotational state energies:

$$E_J = \frac{\hbar^2}{2I} J(J+1) - \frac{4}{\omega_e^2}\left(\frac{\hbar^2}{2I}\right)^3 J^2(J+1)^2, \qquad J = 0,1,2,\ldots$$

To simplify the analysis of experimental data, it is customary to express the energies in term values ($E/\hbar c$) units and substitute the rotational constant $B = h/(8\pi^2 cI)$ and distortion constant D (all constants in the distortion term) to obtain:

$$G_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2, \qquad J = 0,1,2,\ldots$$

If the molecule has a permanent dipole moment, transitions between rotational states J and $J+1$ are allowed. For non-dipolar molecules (e.g., CS_2 or benzene), only Raman transitions between states J and $J+2$ are allowed. This requires an anisotropy of the molecular polarizability (i.e., the molecule is more polarizable along one axis than another). You can readily predict transition energies by calculating the difference energy between pairs of states with corresponding J values.

Your Assignment

It is your assignment to try and analyze carbon disulfide (CS_2) signals in at least 5 different CRASY data sets before your Lab Course Day (Tue or Wed.). On your Lab Course Day, we will have a Zoom meeting to discuss progress and problems and you have to review the analysis of five data-sets analyzed by one of your colleagues and analyze an additional 5 data sets. You have to document your analysis results in the Google Docs sheet here (and linked from Blackboard) and write a report.

Your Data Analysis

Due to the novelty of the CRASY experiment, we develop our own analysis software, concurrently with the experimental development. The analysis program you will use is written in the Python programming language. You can run a compiled windows version or install a Python development environment and run the program from its source code. Links to the compiled program and source code are available for download on Blackboard. If you want to understand more about each step of the data analysis, you can run Python code for a manual step-by-step data analysis as documented on figshare: https://figshare.com/articles/CRASY_data/5886406.

1. Install and run the data analysis program

To install and run the data analysis software, perform the steps outlined as Option (A) or Option (B) below. A video walk-through can be found on BB. If you have already installed Python / Anaconda on your computer (see lab module of Geunsik Lee), you can skip point (B, ii).

Option (A): Download crasyPlots.exe and run it on a Windows computer.
(The executable was tested on several computers running Windows10.)
Please be patient when loading the program, it contains all the Python dependencies and it takes ~20 seconds to load on my computer.

Option (B): Download the Python code and run in in a Python environment.
(The code was tested on 64-bit Windows10 and 32-bit MXLinux.)

i. Download crasy_distribution.zip and extract it to a directory (let's call it <YourDirectory>).

ii. Download and install the python distribution "miniconda" from https://docs.conda.io/en/latest/miniconda.html.
I suggest you select the following install options: *Install For: Just Me*, and *Add Miniconda3 to my PATH environment variable*.

iii. On Windows, open the file explorer and navigate to <YourDirectory>. You should see several python files, e.g., crasyPlots.py. In the file explorer address bar, type "cmd" to open a terminal. (Note: If you didn't select *Add Miniconda3 to my PATH environment variable* during installation, you must instead open an *Anaconda Prompt* from the start menu and then navigate to <YourDirectory> using change directory (cd) commands). On Linux or Mac, open a terminal window and navigate to <YourFolder>.

iv. Install the required Python packages numpy, scipy and pyqtgraph. Type in the terminal:
conda install numpy scipy pyqtgraph

Next you can run the data analysis program with the command:
python crasyPlots.py

When the data analysis program runs, you will see one window with a graphical user interface (UI, mostly white) and another that will show all status messages of the underlying Python script (mostly black). You can ignore the latter.

2. Perform the Data Analysis

To perform the data analysis, you must extract a rotational spectrum from an experimental data-set and fit CS_2 rotational constants to observed transition frequencies. I posted a video walking you through the analysis steps on Blackboard and I give you step-by-step instructions below. Start the measurement program as described above. Fig. 5 marks the location of critical elements in the UI. Hover the mouse over UI elements to see tool-tips.

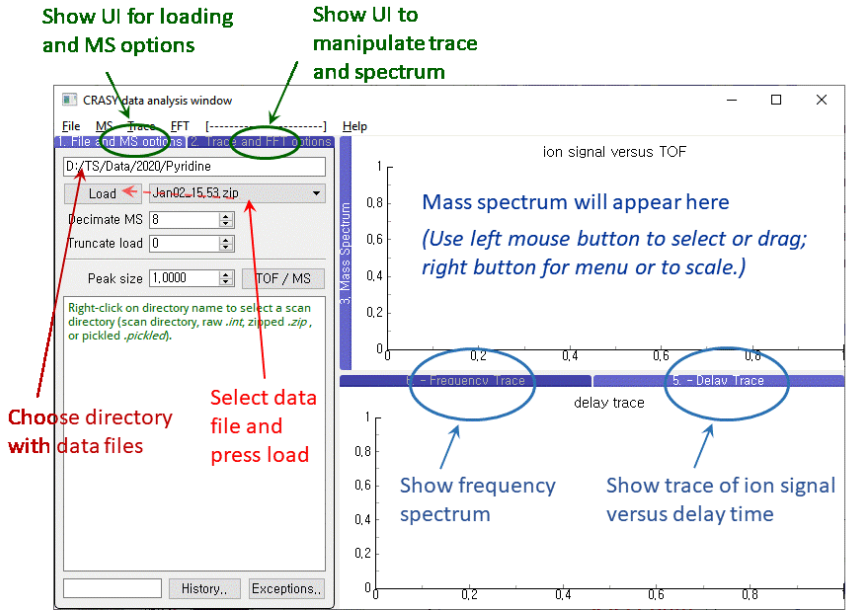

Fig. 5: Important UI elements in the CRASY analysis program.

- ***Load measurement data***

Download five or more measurement files from Blackboard. Data files are zipped and sorted by year and date. The filenames reflect the measurement date and time (a typical filename is: */2018/Jul23_17.57.zip*). To load a file, you must first enter the name of the directory containing the measurement files (see Fig. 5). This updates the file list in the row below and you can then select a data file and press load. Note that you must open a new analysis program instance for each data file; you cannot load a new data file over an old one. The data files contain many mass spectra in compressed format and loading may take some time.

- ***Identify the CS_2 mass signal and plot the FFT spectrum***

Fig. 6 show the analysis window after loading a data file. The mass axis is not initially calibrated. You can try to calibrate (see video guide), but this is not required. If you want to reload the data set at a later time, then it might be worthwhile to save the data as 'pickled' file (file menu -> save pickled). Loading pickled data is much faster than loading compressed data.

In the plotted data windows, you can hold the right mouse-button to zoom into the plot and hold the left mouse button to move the plot. If you select the shaded region between cursors, you can move the cursor boundaries, e.g., to change the integration boundaries for a mass signal.

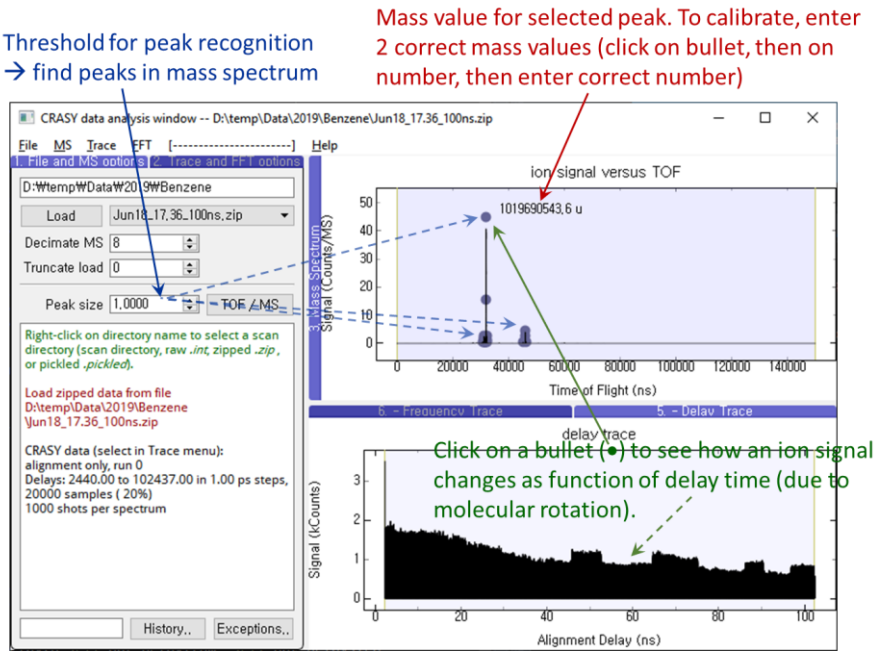

Fig. 6: Identifying mass peaks and plotting time-dependent ion signals.

A left mouse-click on the bullet above a mass peak will plot the delay trace and frequency spectrum for that mass. Now switch over to the UI tab *2 Trace and FFT options* and also switch to tab *6 - Frequency Trace* to show the frequency spectrum (see Fig. 5 for UI elements). Figure 6 shows the UI elements that allow you to manipulate the time-dependent ion signal trace before Fourier-transformation. These manipulations are helpful to generate a nice spectrum. Plot the normalized power spectrum for better clarity. Then correct the baseline; a cosine windowed (cosw) or square windowed (sqw) baseline correction with 100-point window size usually works well. Increase the padding factor for a smooth interpolation of spectral points, e.g., to a value of 8.

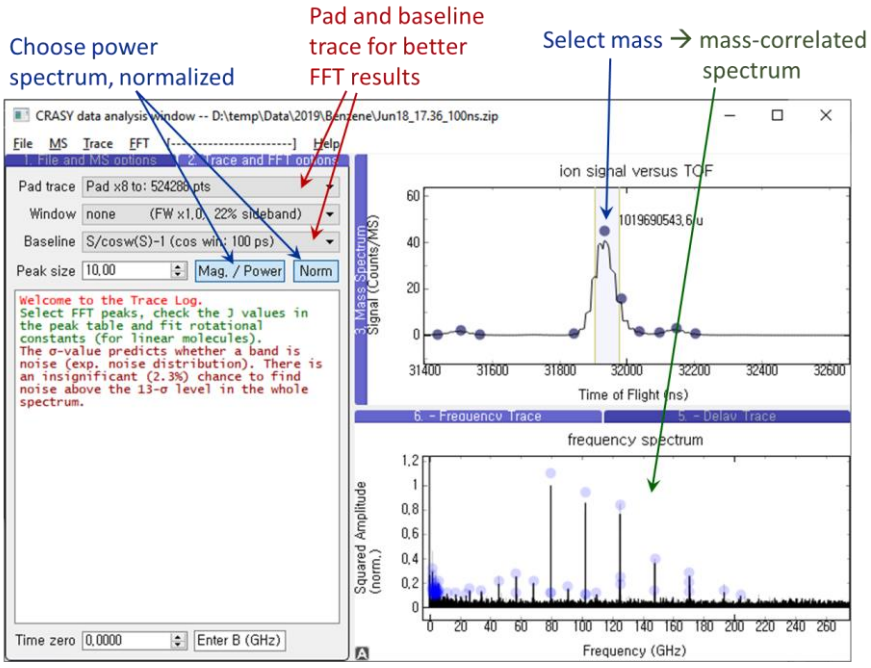

Fig. 6: Generating a rotational spectrum by Fourier-analysis of a time-dependent mass signal.

- ***Assign rotational Raman transitions***

To identify the CS2 spectrum, you can use the mass information if the MS is calibrated, or you can compare the rotational spectra to known spectra for the chemical species you expect. The rotational spectrum of CS2 is very simple, because it is a linear rotor: we expect a single progression of linearly spaces transition frequencies. Fig. 7 compares the spectra of benzene and CS_2, illustrating the difference between a linear rotor spectrum (CS_2) and the spectrum of an oblate top (benzene). Compare the spectra with that in Fig. 6 and you should recognize that Fig. 6 shows a benzene spectrum.

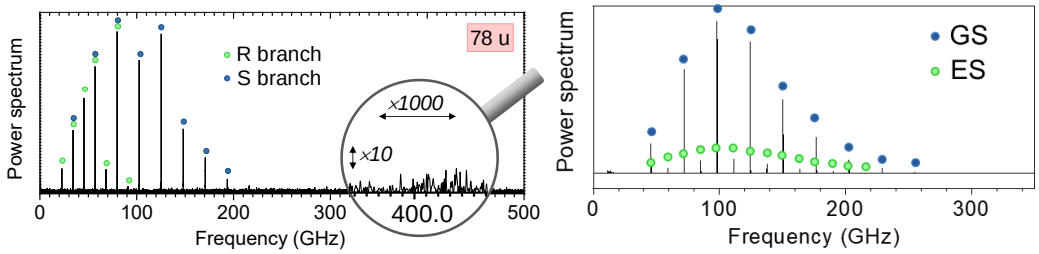

Fig. 7: (Left) rotational Raman spectrum of benzene, showing distinct progressions for the R and S branch. (Right) Rotational Raman spectrum of CS_2. In the CS_2 spectrum, a smaller progression from a vibrationally excited state (ES, green dots) is observed; in most spectra this progression is absent or very weak..

If your frequency spectrum does not resemble the expected CS_2 spectrum, you should check the spectra associated with other mass peaks. In most data-sets, we measured other chemical compounds and only trace quantities of CS_2 were present for calibration, so only a small mass signal might stem from CS_2. Next, it is time to assign and fit the rotational transition frequencies. The program can automatically assign transition lines if you enter the expected transition frequency (see: Fig. 8). The literature rotational constant is B = 3.271 517 GHz and entering a value of B = 3.27 should identify most CS_2 lines or lines in close proximity. You must check the lines to avoid spurious assignments: we expect the strongest (highest) peaks to be real transitions; the program might pick nearby weaker lines that are sidebands or noise. Click on the red bullets that mark transition lines to remove / replace spurious assignments.

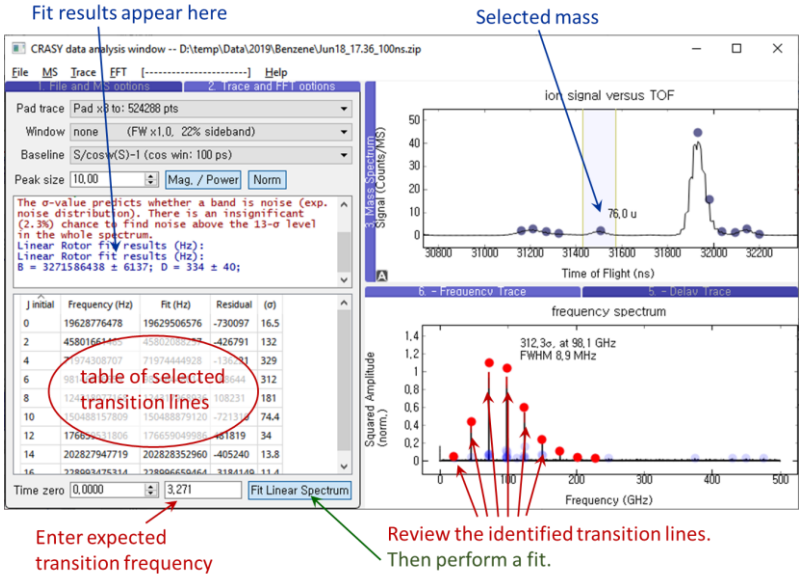

Fig. 8: Selecting, reviewing, and fitting of transition lines.

- ***Fit the assigned transition frequencies***

When you press "Fit Linear Spectrum", all selected line positions (marked by red bullet points and listed in the table of transition lines) are fitted to the expected positions for a linear rotor. The fit results are the rotational constant B and the distortion constant D. Check how the uncertainties change if you modify the line assignments (only a minimum of 3 assigned lines is required for a fit). You can also test how other options affect the fit result. As illustrated in Fig. 9, the expected fit uncertainty in B is expected to be significantly below the spectroscopic resolution if the line assignments are correct.

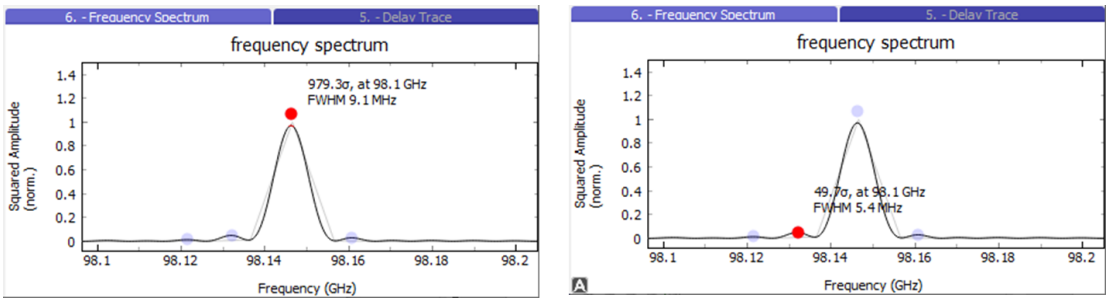

Fig. 9: (Left) Zoom into a single line of a CS_2 spectrum from a 100 ns delay scan shows a full-width-at-half-maximum (FWHM) resolution of 9 MHz. The fitted rotational constant based on 8 assigned lines in this spectrum was B = 3271587268 ± 2957 Hz and, the ~3 kHz uncertainty in B is far below the 9 MHz resolution. The wrong assignment of this one band increases the uncertainty by almost an order-of-magnitude to B = 3271587651 ± 21638.

Once you are confident that all your assigned lines are correct and that you performed the best possible fit, copy your results into the online Google Docs table linked from the blackboard contents section at and note them for your report. Also note any significant observations about the data-set you analyzed, e.g., about the magnitude of CS_2 signal in the data-set, the quality of the spectrum, whether the spectroscopic resolution was in the expected range, problems you encountered in the assignment and fitting of the spectrum, etc. Paste your most-important comments into the online table to facilitate the work of others who might look at the same data set.

Report

For your report, please write a one-paragraph *Introduction* summarizing your understanding of the CRASY method. Then describe your analysis of 5 data-sets in a *Results* section. Include a table summarizing your results (cf. Table 1 for formatting). State clearly whether your file contained sufficient CS2 signal for a meaningful fit, what parameters you used to obtain your final fit results and how well your results agreed with the literature values. State the scan delay range and the spectroscopic resolution. We expect a spectroscopic resolution close to $\Delta\nu = 1/t_{range}$ and a fit uncertainty well below that. (I.e., a resolution of $\Delta\nu \approx 10$ MHz and 500 MHz for the first and second row of Table 1.) *Discuss* particular or surprising observations you made.

Table 1: Fit results for CS2 signal in analyzed CRASY data sets. All frequencies in Hz.

Name	B	D	$(B/B_{Lit.})-1$	Comments
Jun18_17.36_100ns.zip	3271586438 ± 6137	334 ± 40	2.12e-5	200 ns scan, benzene and some CS_2. Good CS_2 spectrum.
Jul20_12.01.zip	3271178145 ± 58303	1298 ± 343	1.04e-4	2 ns scan, only CS_2. Good CS_2 spectrum.