Systematic study of ^{223}RaF from the 2023 campaign

Proposal by
M. Athanasakis-Kaklamanakis, S. Wilkins, R.F. Garcia-Ruiz
INTC-P-555-ADDENDUM

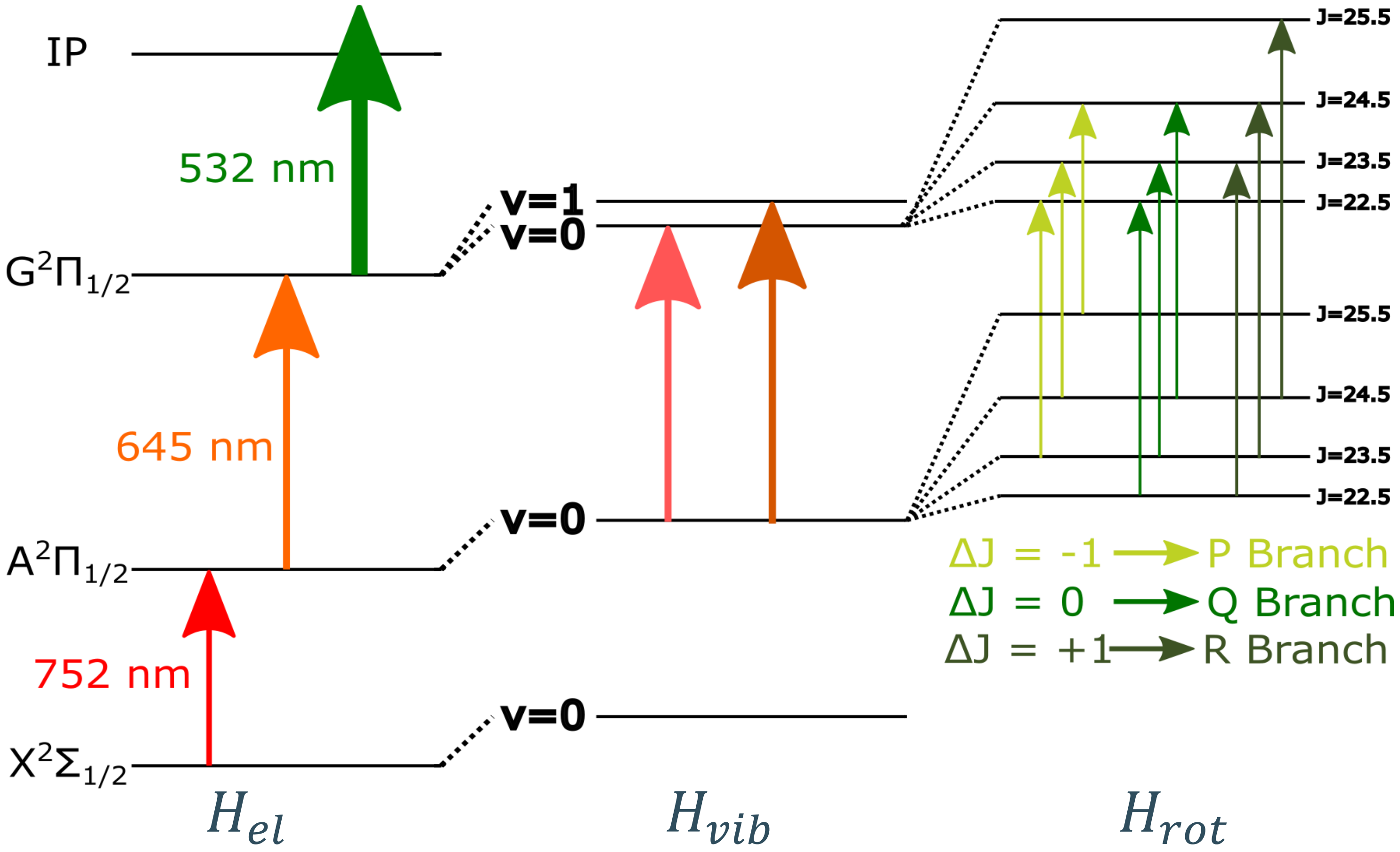
PhD student: Carlos M. Fajardo-Zambrano

CRIS collaboration meeting, January 2025.

Quick introduction

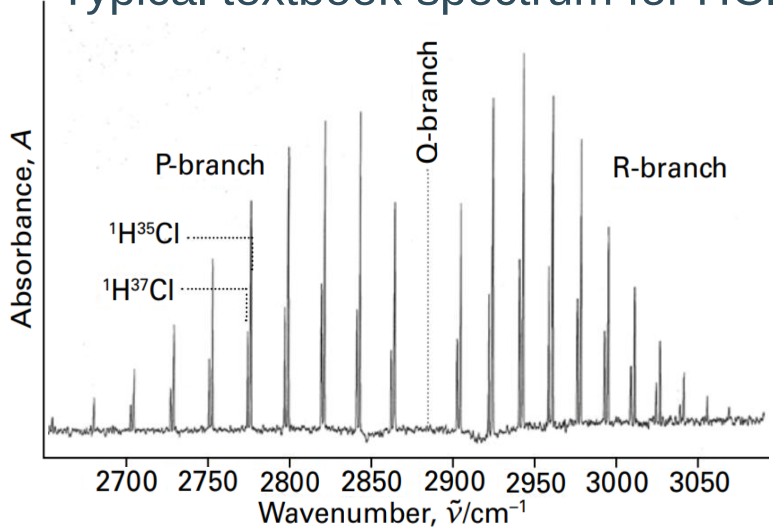
Laser spectroscopy on molecules

The spectrum of a rovibrational transition is divided in three different branches: R ($\Delta J = +1$), Q ($\Delta J = 0$), P ($\Delta J = -1$).



Each rotational line is further split due to the electron-nuclear interaction (H_{hfs}).

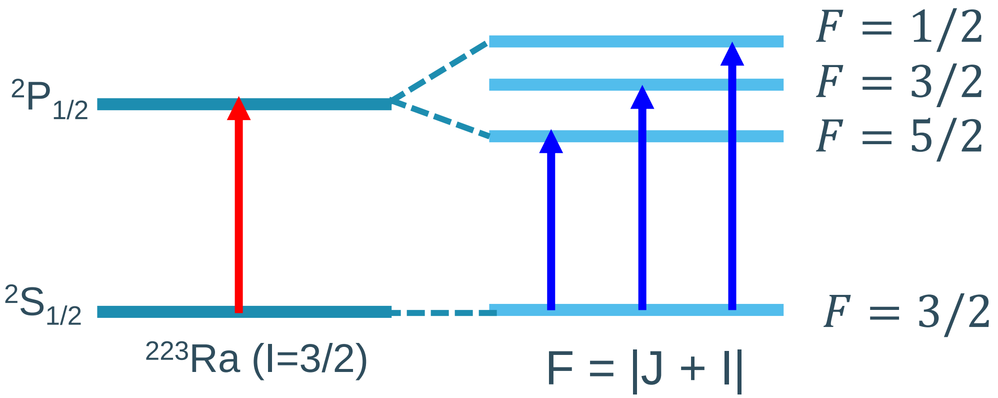
Typical textbook spectrum for HCl

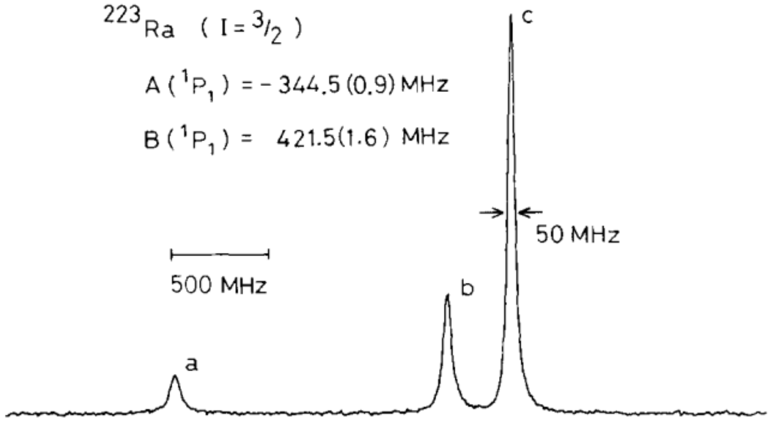


[1] Atkins, Physical chemistry, P. Atkins, P. W., & de Paula, J. (2014).

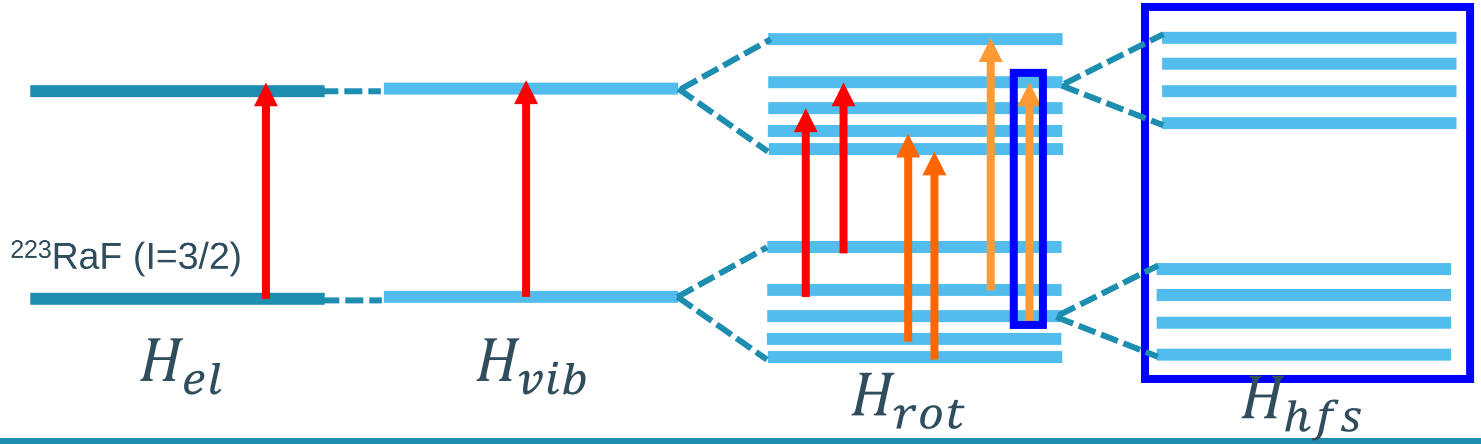
High-resolution in atoms and molecules

$$H_{hfs} = H_m + H_Q = A(I,J) + B(I,J)$$





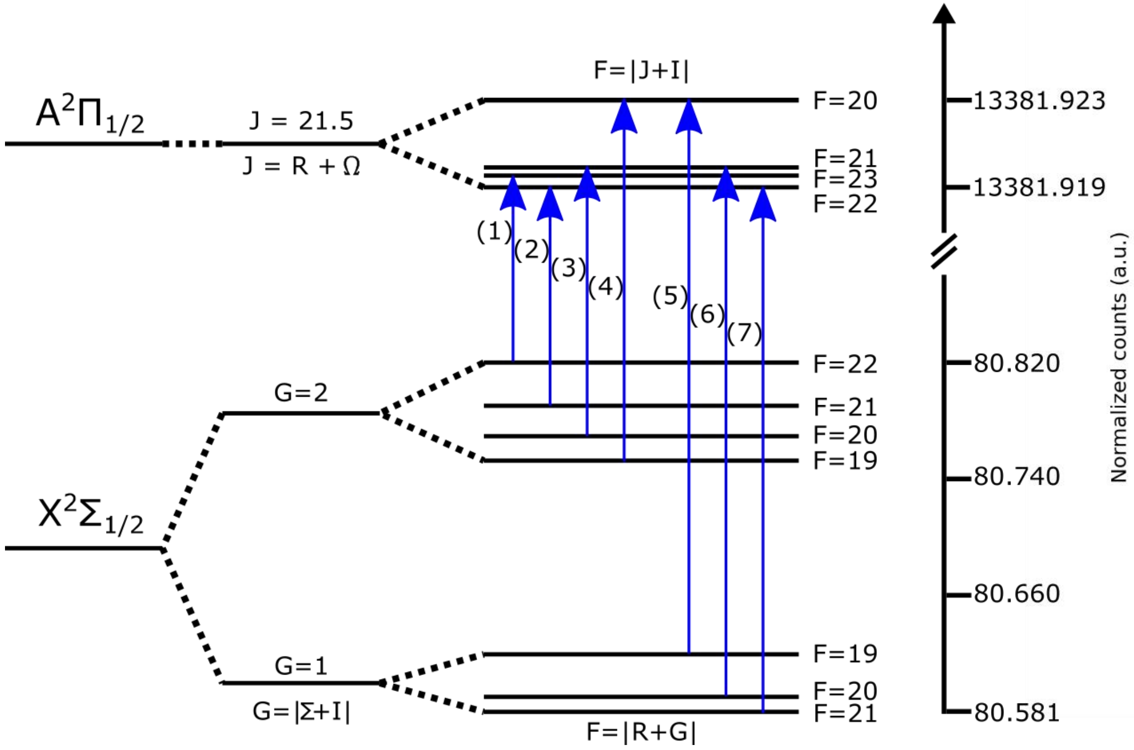
$$H_{hfs,R} = H_m + H_Q = A_{\parallel}(I_z,J_z) + A_{\perp}(I_{(x,y)},J_{(x,y)}) + eq_0Q(I_z,J_z) - eq_2Q(I_{(x,y)},J_{(x,y)})$$

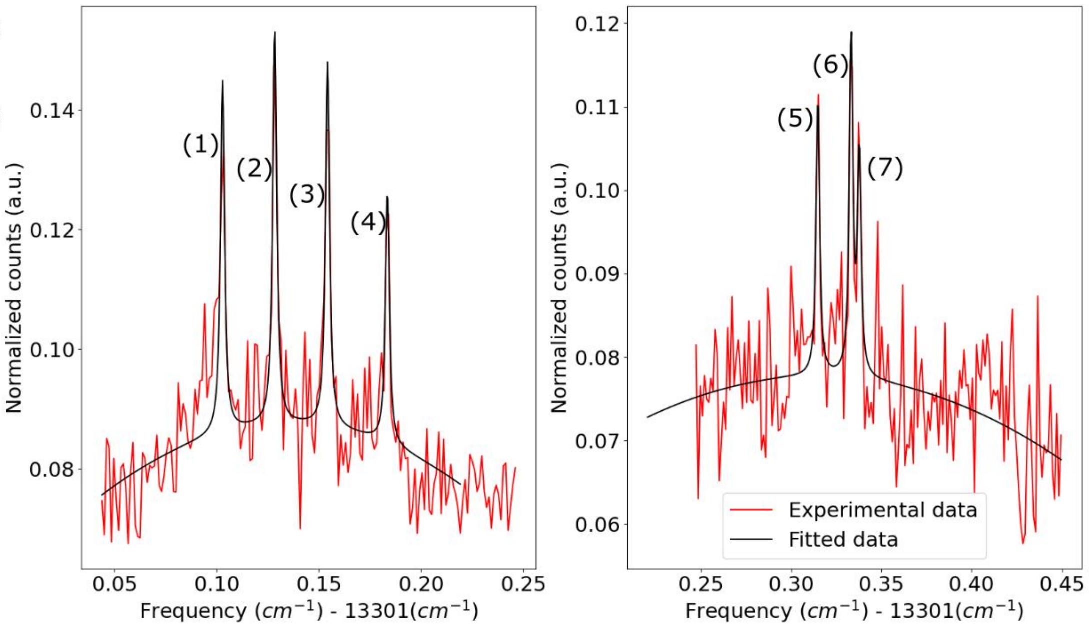


Each rotational transition is one HFS spectrum of ^{223}RaF like the one above

[2] Ahmad, S. A., et al. Physics Letters B 133.1-2 (1983): 47-52.

High resolution ^{223}RaF (I =3/2) spectrum (R-branch)





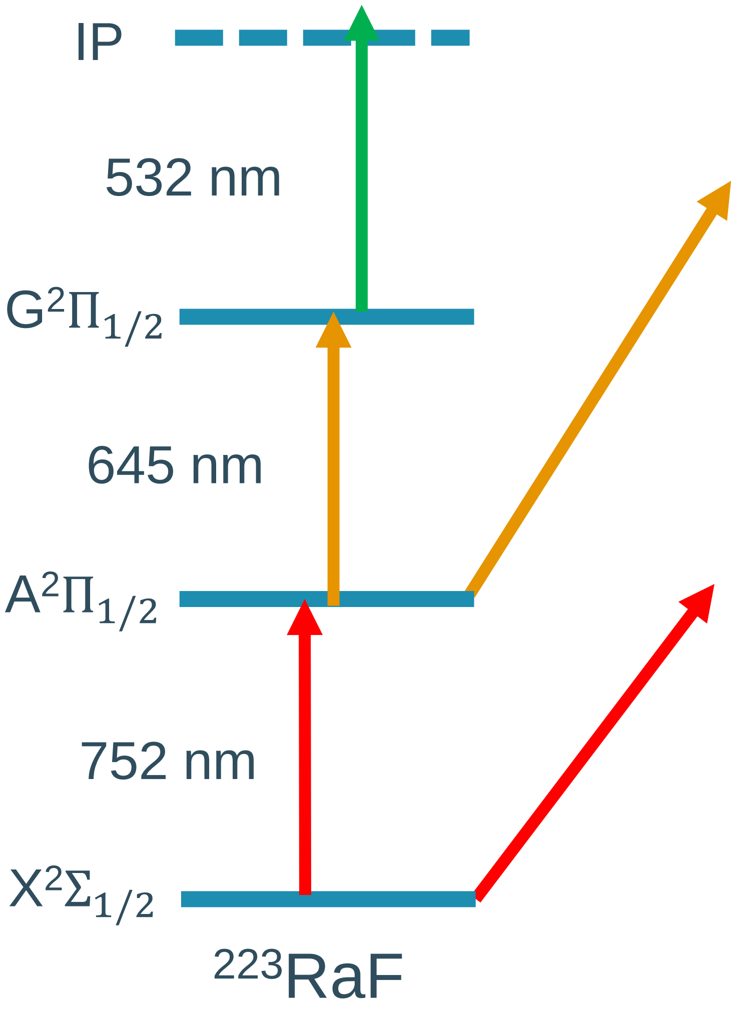
Frosch and Foley molecular constants

$$H_{hfs} = H_m + H_Q = a(I,L) + b_F(I,S) + c(I,S) + d(S_+I_+,S_-I_-) + eq_0Q(I,S) - eq_2Q(S_+I_+,S_-I_-)$$

- a: is the nuclear spin-electron orbit interaction ($\Lambda \neq 0$ ➔Π, Δ states).
- b_F: is the Fermi contact interaction ($\Sigma \neq 0$).
- c and d are the nuclear spin-electron spin axial ($\Sigma \neq 0$) and perpendicular dipole interaction ($\Lambda \neq 0$ ➔Π, Δ states).
- eq_0Q and eq_2Q are the nuclear quadrupole axial ($\mathrm{I} > 1/2$) and perpendicular coupling constants ($\Lambda = 1$ ➔some Π states).

$$\Sigma(\text{molecules}) \leftrightarrow S(atomic) \qquad \Lambda(\text{molecules}) \leftrightarrow L(atomic)$$

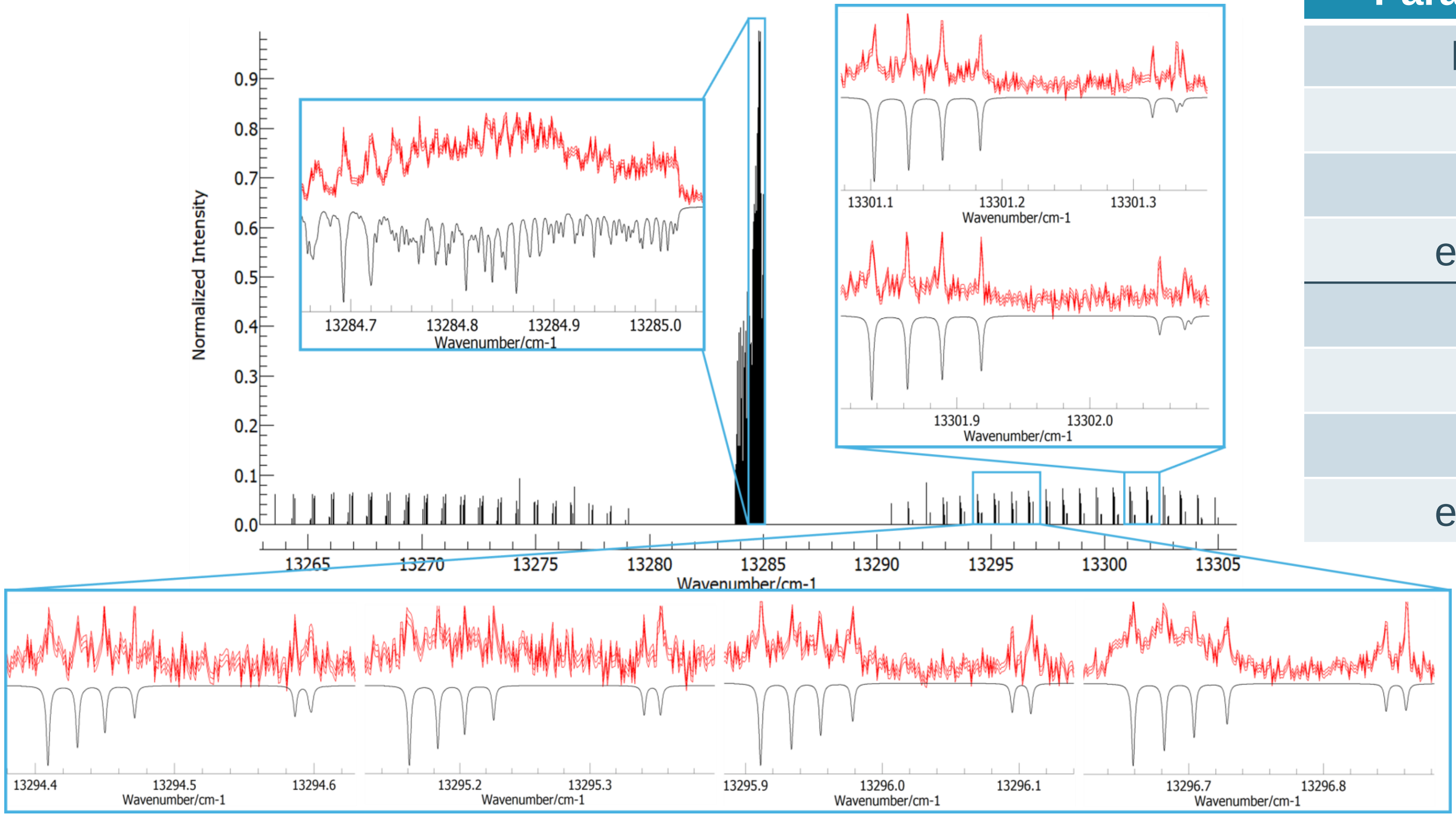
The ^{223}RaF case



- Electronic parameter: T_Π, B', D', p and p_d
- Nuclear parameters: $\underbrace{a, b, c,}_{\text{Not-constrained}}$ d and eqQ_0

- Electronic parameter: B'', D'', γ
- Nuclear parameters: b, c and eqQ_0

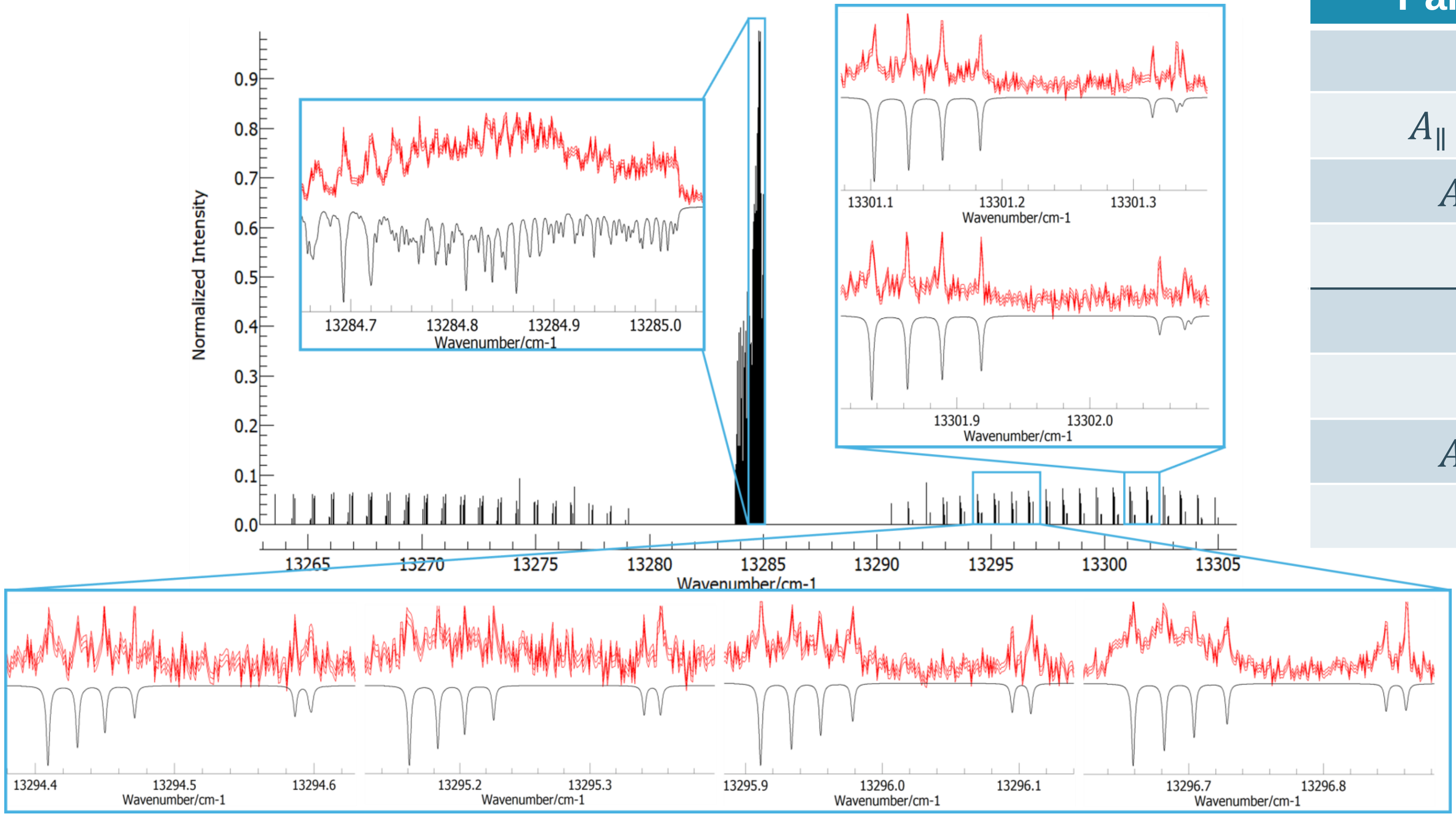
Fitting of the ^{223}RaF spectra (PGOPHER).



Parameter	Value (std)[sys]
B’’	5761.557(30)[7]
b	2029.0(20)[5]
c	53(7)[2]
eqQ	-1472(25)[5]
T	13284.69751(10)[2]
B’	5731.958(30)[7]
d	251.5(20)[3]
eqQ	-939(21)[4]

Total of 6 R-branch lines were measured ➔ 6 HFS spectra.

Fitting of the ^{223}RaF spectra (PGOPHER).



Parameter	Value (std)[sys]
B''	5761.557(30)[7]
$A_{\parallel} = b + c$	2082(7)[2]
$A_{\perp} = b$	2029.0(20)[5]
eqQ	-1472(25)[5]
T	13284.69751(10)[2]
B'	5731.958(30)[7]
$A_{\perp} = d$	251.5(20)[3]
eqQ	-939(21)[4]

Fitting procedure:

- Initial R-branch fit
- Fit including the Q-branch

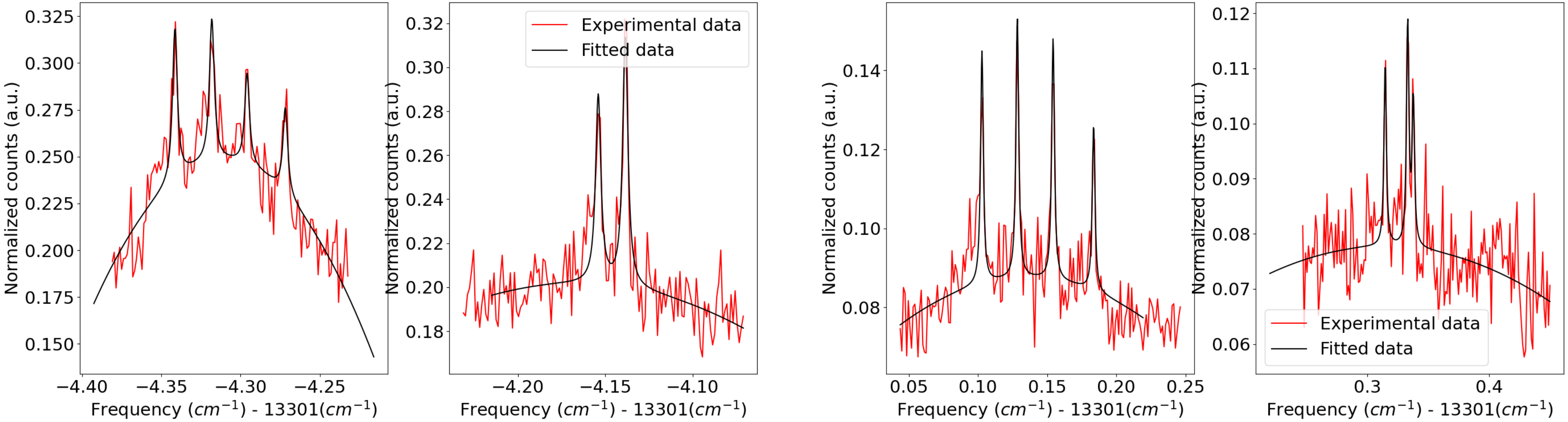
Assumptions for the initial fit

- Electronic molecular constants are taken from ^{226}RaF fitting and are **not modified (γ and p).**
- The rotational constants **(B'', B') were scaled** from ^{226}RaF using the reduce mass.
- Given the high correlation with $B''$and B', the centrifugal distortion constant **(D_e'', D_e') are left as constants** (also scaled using the reduce mass).
- Initial energy taken from broadband isotope shift measurements on RaF.
- Molecular **HFS constants are scaled** from ^{225}RaF theoretical predictions.
- The **eqQ are taken from Leonid's** calculations on ^{223}RaF.

Linewidth determination

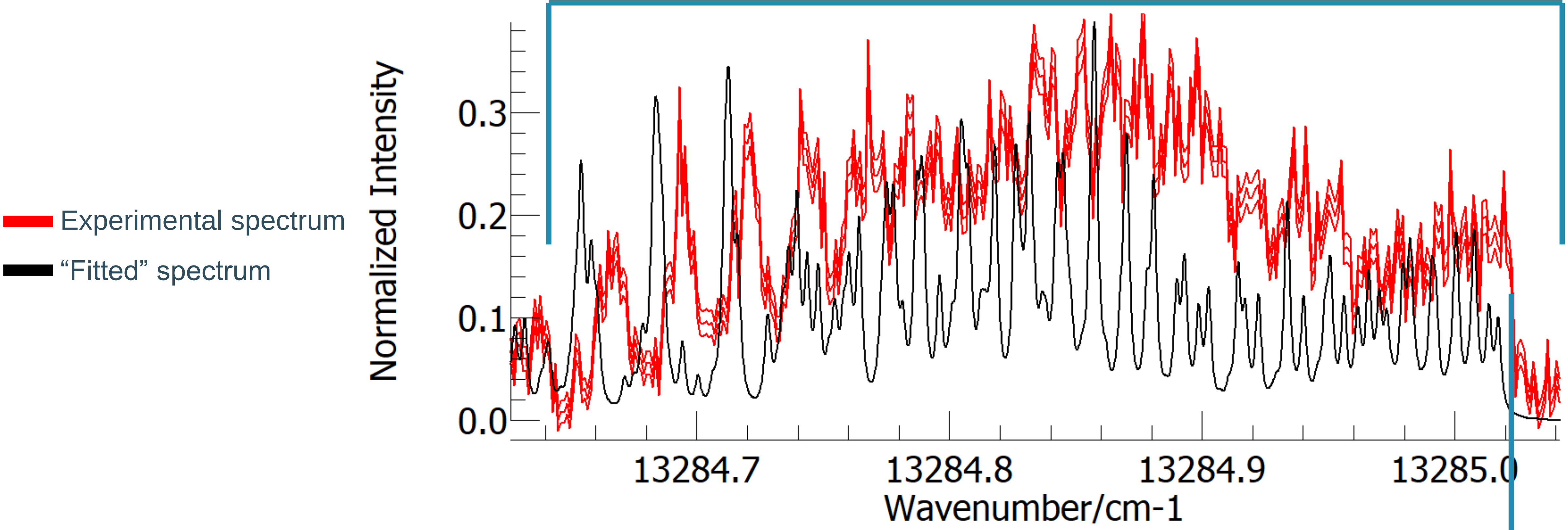
To define the linewidth of each of the HFS peaks, the peaks were fitted using SATLAS 2.

Such fitting allow the inclusion of the bkg (taken as a polynomial of second order). The error on the peaks center ranges between ~3 and ~21 MHz.



Q-branch unconstrained, R-branch fitted

Q-branch dependent on the J levels included

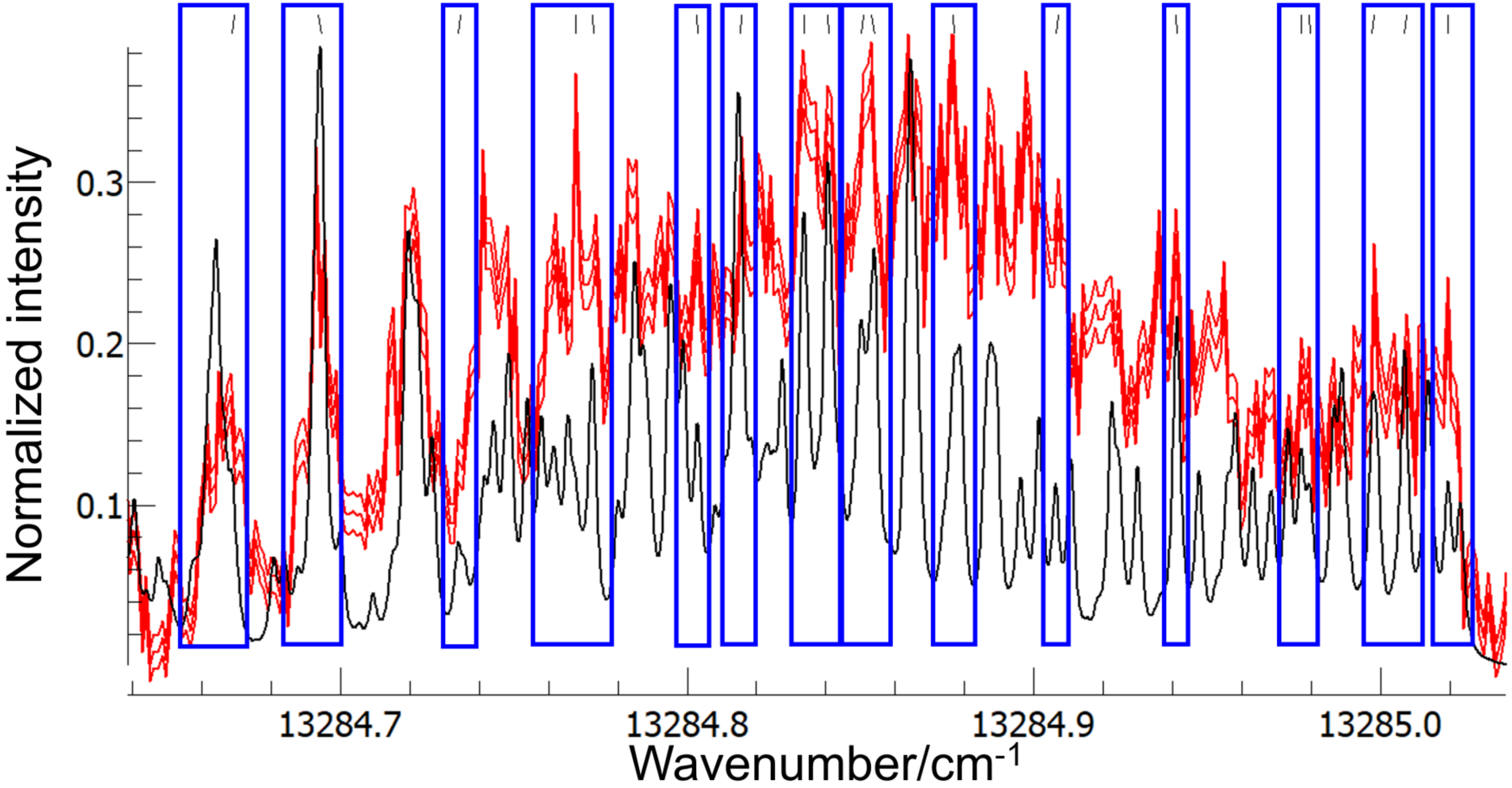


Band head

- The initial fit (R-branch) gives an idea of the peaks to be fitted in the Q-branch.
- The Q-branch needs to be included to constraint the fit (E, B’, B’’).

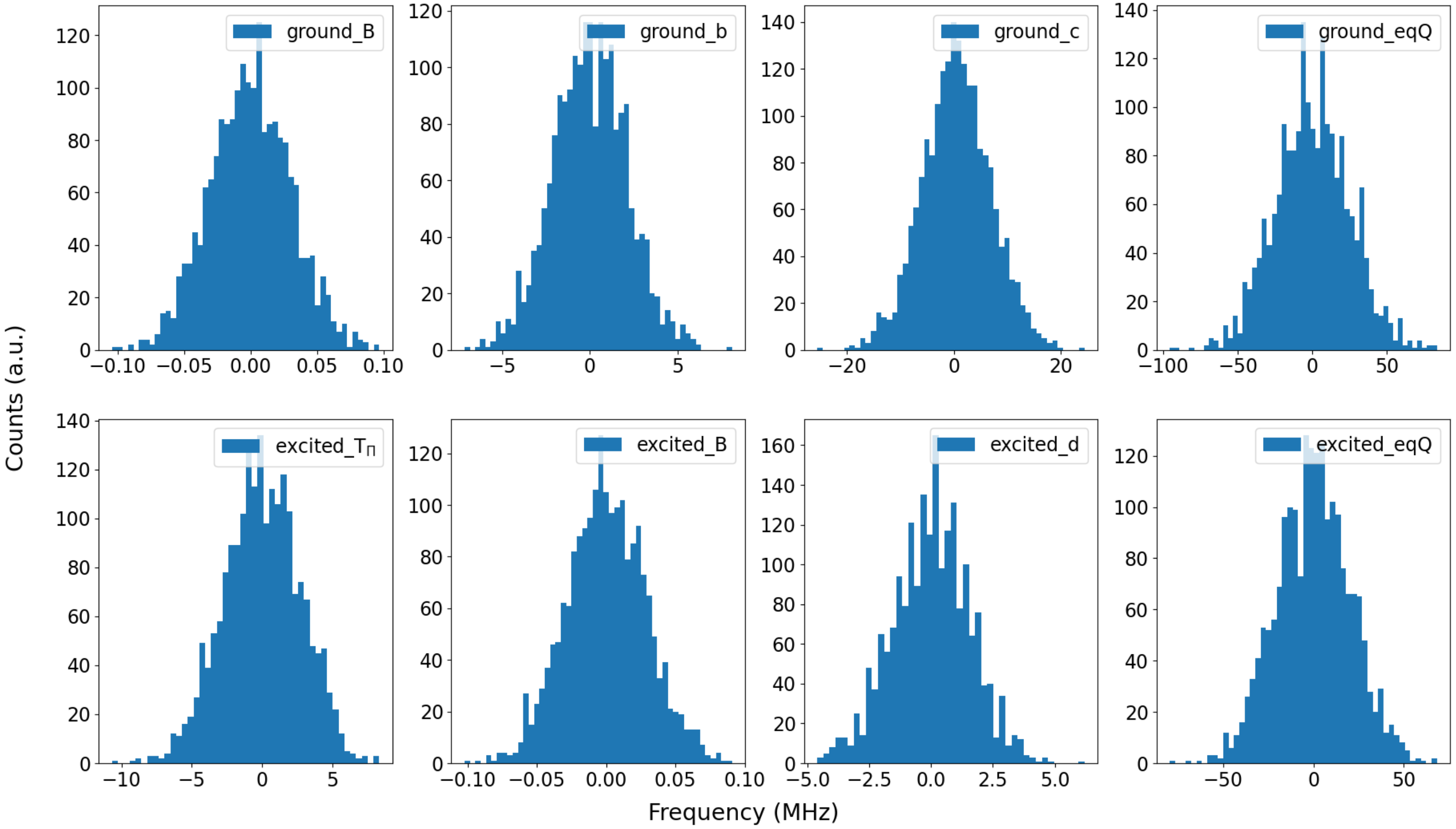
Peaks taken from the Q-branch

19 arbitrary peaks were selected. These peaks are needed to constrain the rotational constants and the energy of the excited state.

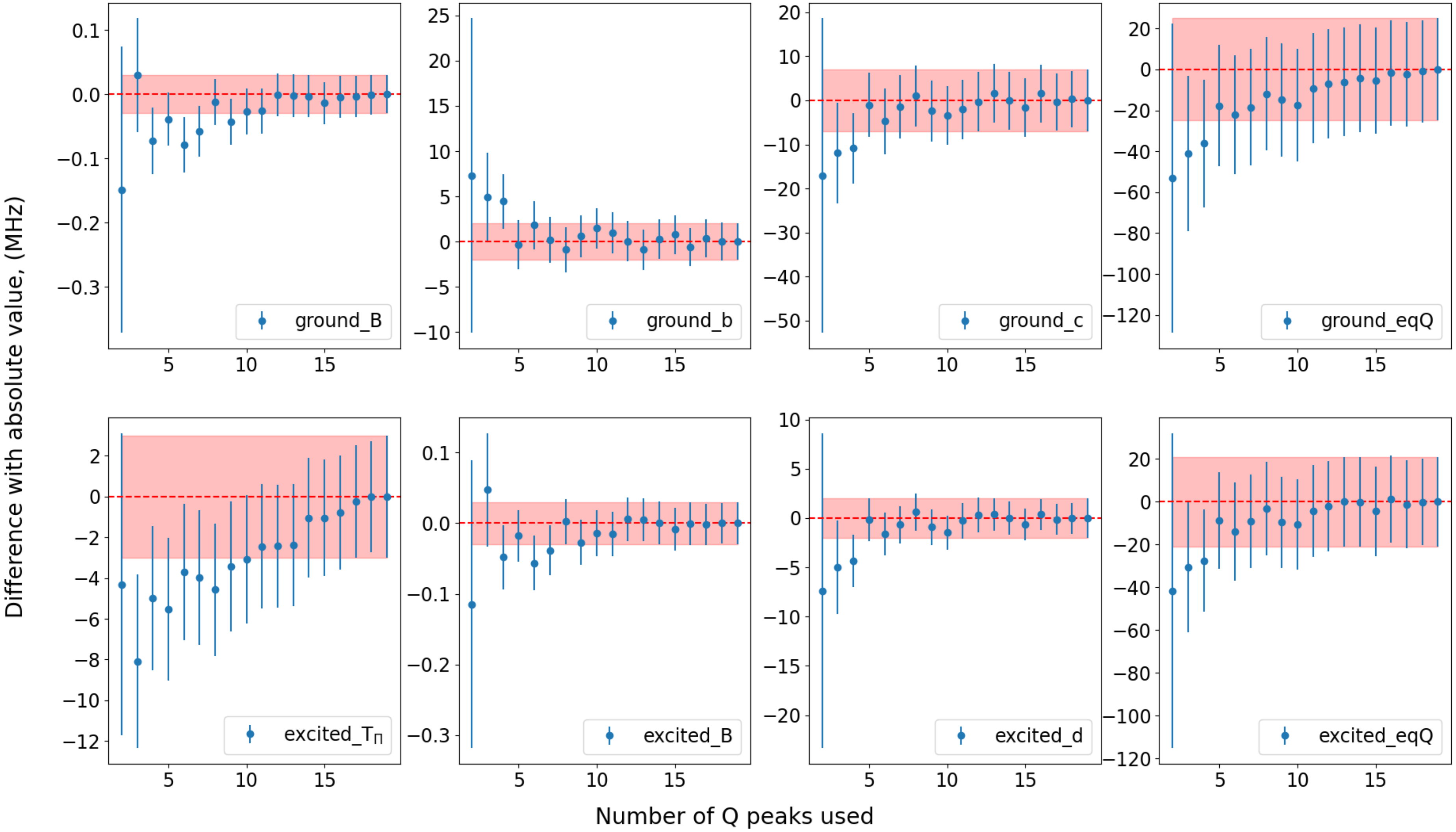


Final fit and estimation of statistical errors

- Once the fitted spectrum matched the experimental data, the fitting was automatize using Python.
- Based on the uncertainty in each HFS peak, a Gaussian distribution was created: (centroid = HFS peak centroid) and (width = HFS peak uncertainty).
- Re-fitting of the spectra with new peak centroids taken from the Gaussians.
- Store the fitted molecular constants and re-fit the spectra (total = 5000).
- The retrieved distribution from each constant gives its nominal value and uncertainty.

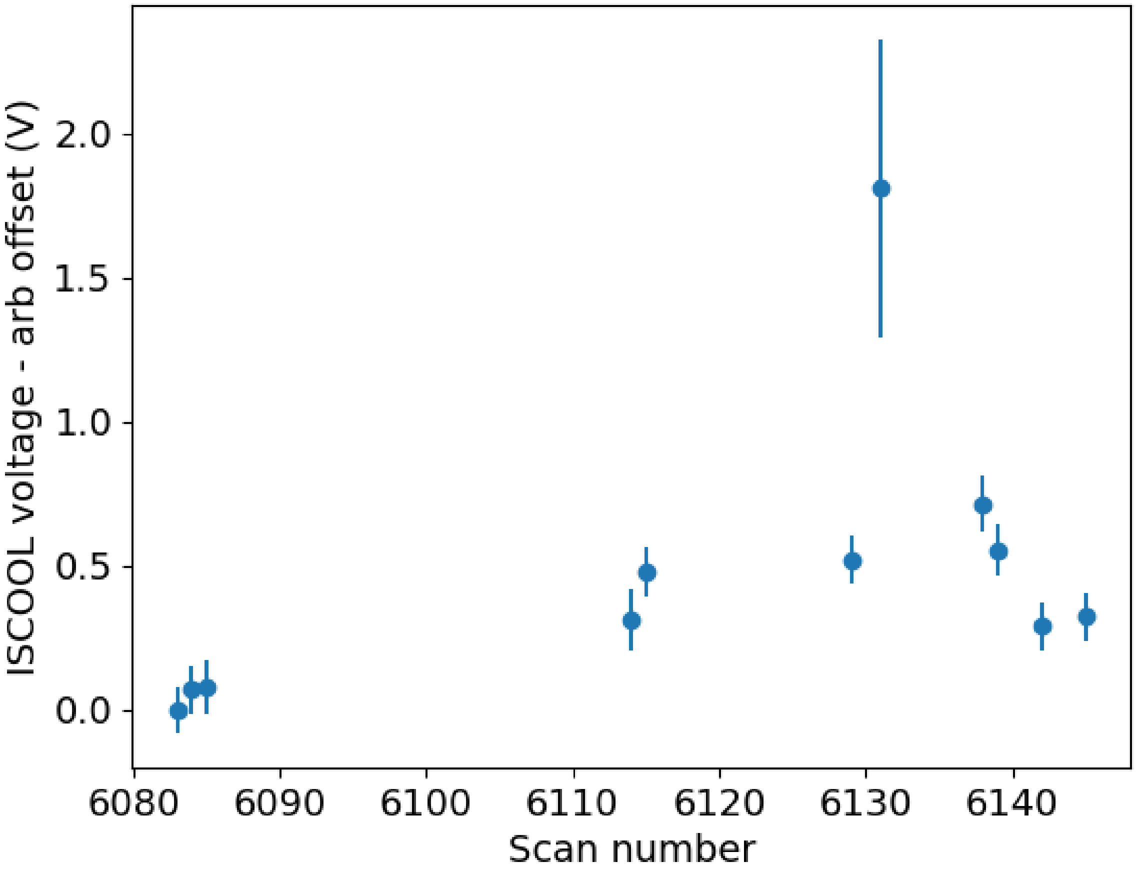


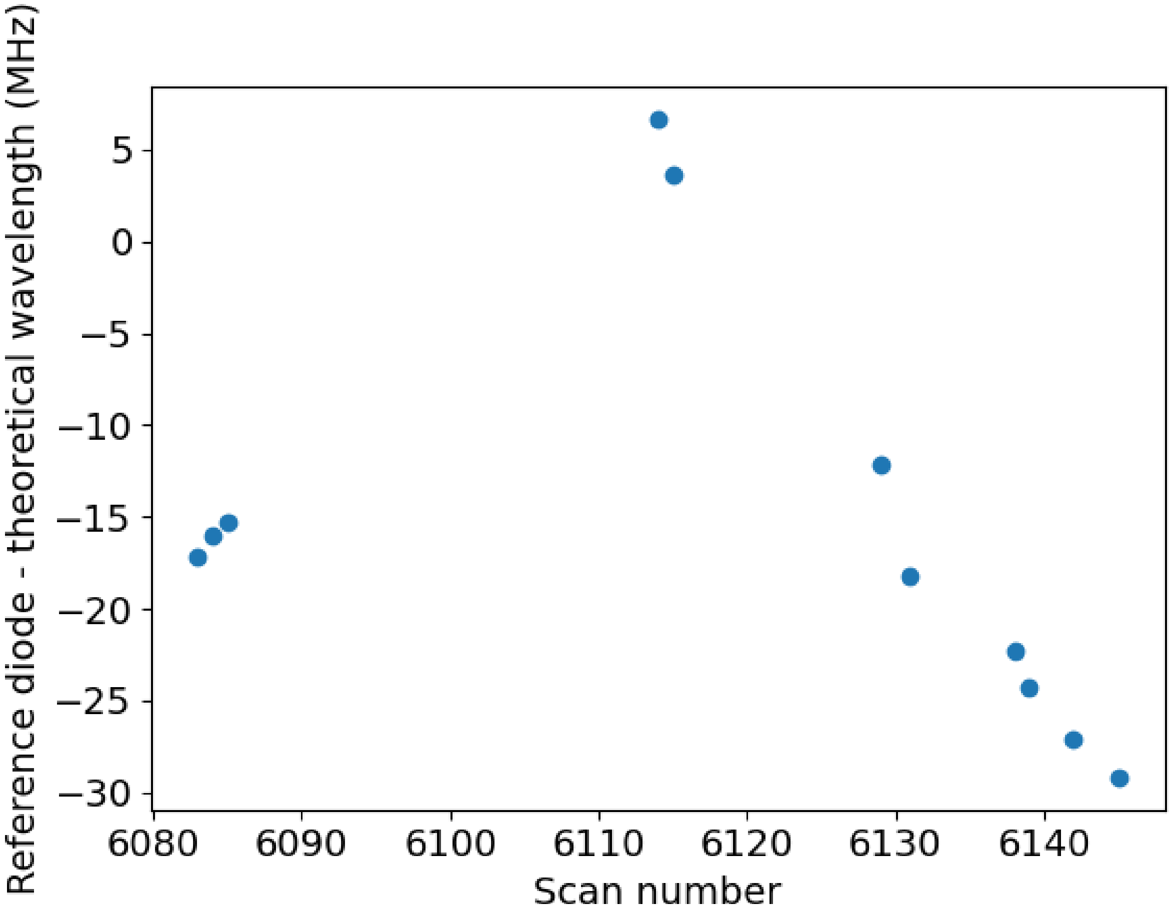
Molecular constants with Q lines (mean)



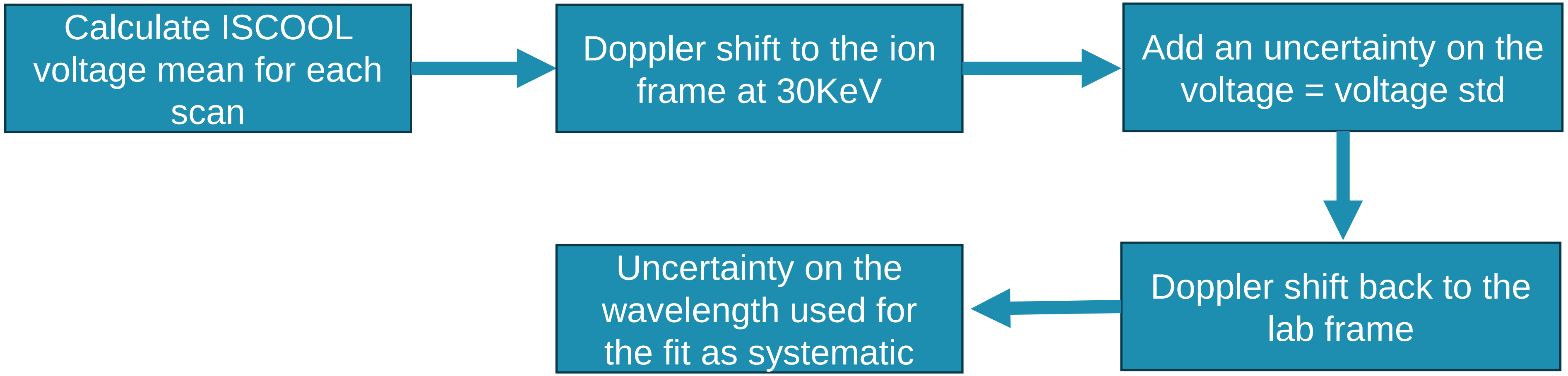
Systematic error

ISCOOL voltages and reference diodes across scans





ISCOOL voltage systematic error contribution



Calculate ISCOOL voltage mean for each scan

Doppler shift to the ion frame at 30KeV

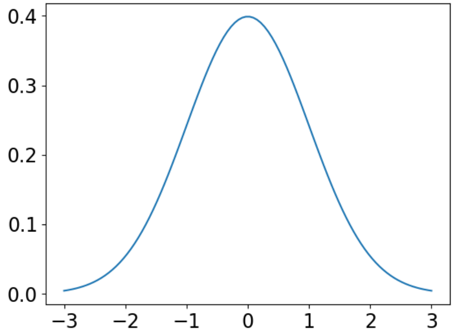
Add an uncertainty on the voltage = voltage std

Doppler shift back to the lab frame

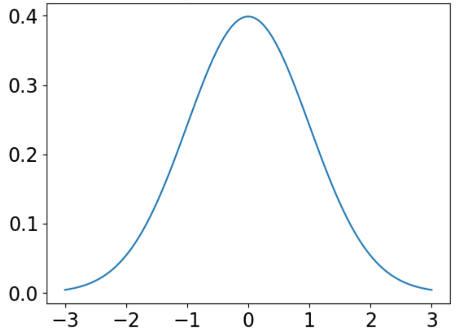
Uncertainty on the wavelength used for the fit as systematic

- This error was obtained individually for each of the 38 peaks on the R-branch
- The same procedure was done for the voltage divider calibration factor

FWHM = centroid uncertainty



FWHM = voltage + diode uncertainties



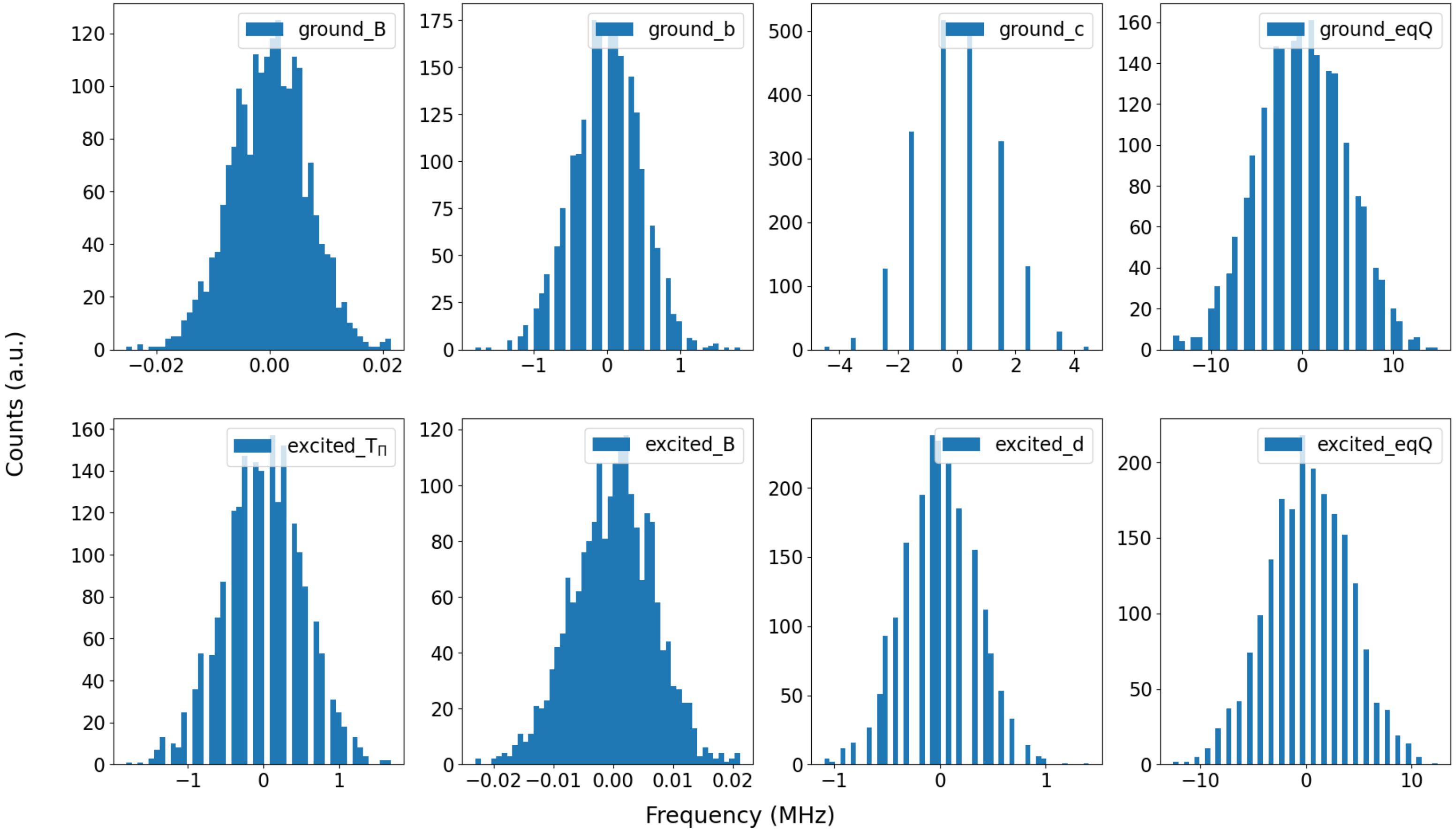
Sources of systematic error (MHz)

Rotational Line	ISCOOL variation	ISCOOL voltage divider	Reference diode variation	Total new peak FWHM
1	0.3	0.5	0.6	1.4
2	0.3	0.5	0.3	1.1
3	0.5	0.5	1	2.0
4	2	0.5	0.9	3.4
5	0.5	0.5	1	2.0
6	0.5	0.5	1	2.0

- Error due to ISCOOL variations were calculated for each individual peak.
- Error due to Reference diode was obtained for the whole rotational line.

Systematic errors on the molecular constants of ^{223}RaF

- Based on the previous uncertainty a Gaussian distribution was created: (centroid = HFS peak centroid) and (width = systematic uncertainty).
- Re-fitting of the spectra with new peak centroids taken from the Gaussians.
- Store the fitted molecular constants and re-fit the spectra using new peak centroids.
- The retrieved distribution from each constant gives its nominal value and uncertainty.



Nuclear moments

Extracting the nuclear moments

We can calculate the EFG of Leonid based on his theoretical eqQ and assumed Q = 1.21.

Ground state EFG$_{theory}$	**Excited state EFG$_{theory}$**
-5.18(28)	-3.20(17)

Extract the electric quadrupole moment **using the predicted EFG (main source of uncertainty).**

Quadrupole moment

EFG

Quadrupole coupling constant

$$Q(^{223}Ra) = \frac{eqQ_{exp}(^{223}RaF)}{q(RaF)_{theo}0.2349647}$$

$Q(^{223}\text{RaF})_{\text{ground}}$ = 1.21(7) b

$Q(^{223}\text{RaF})_{\text{excited}}$ = 1.25(7) b

$Q(^{223}\text{Ra})_{\text{ground}}$ = 1.21(7) b

[3] Petrov, A. N., & Skripnikov, L. V. (2020). Physical Review A, 102(6), 062801.

Extracting the nuclear moments

Similarly, we can extract the magnetic dipole moment **using the known moments of an isotope (^{225}RaF)**

$$\mu_2(A) = \frac{I_2\ A_{2(\parallel,\perp)}}{I_{ref}\ A_{ref(\parallel,\perp)}} \mu_{ref}(A)$$

State	$\mu(A_{\parallel})$	$\mu(A_{\perp})$	**Weighted mean**
$X\ \Sigma_{1/2}(A^0 + A^{BW})$	0.2686(10)[10]	0.2736(6)[7]	0.2722(5)[6]
Atomic	**0.2703(6)[1]**	-	**0.2703(6)[1]**

[4] Lynch, K. M., et al. (2018). Physical Review C, 97(2), 024309.
[5] Wilkins, S., et al. (2023). arXiv preprint arXiv:2311.04121.

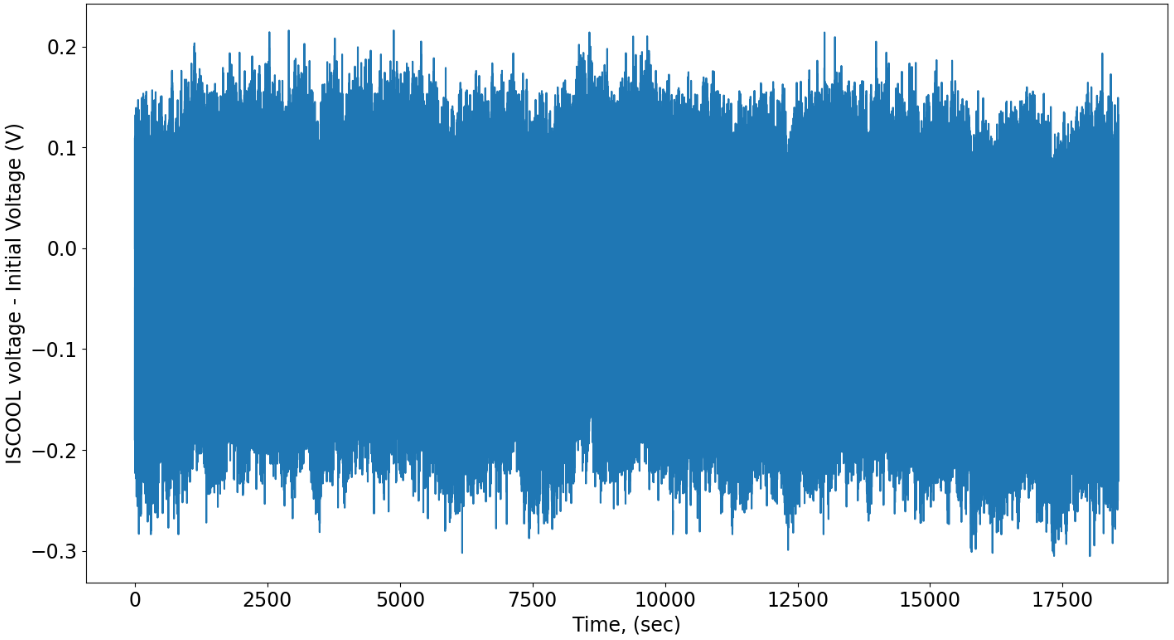
Conclusions and outlook

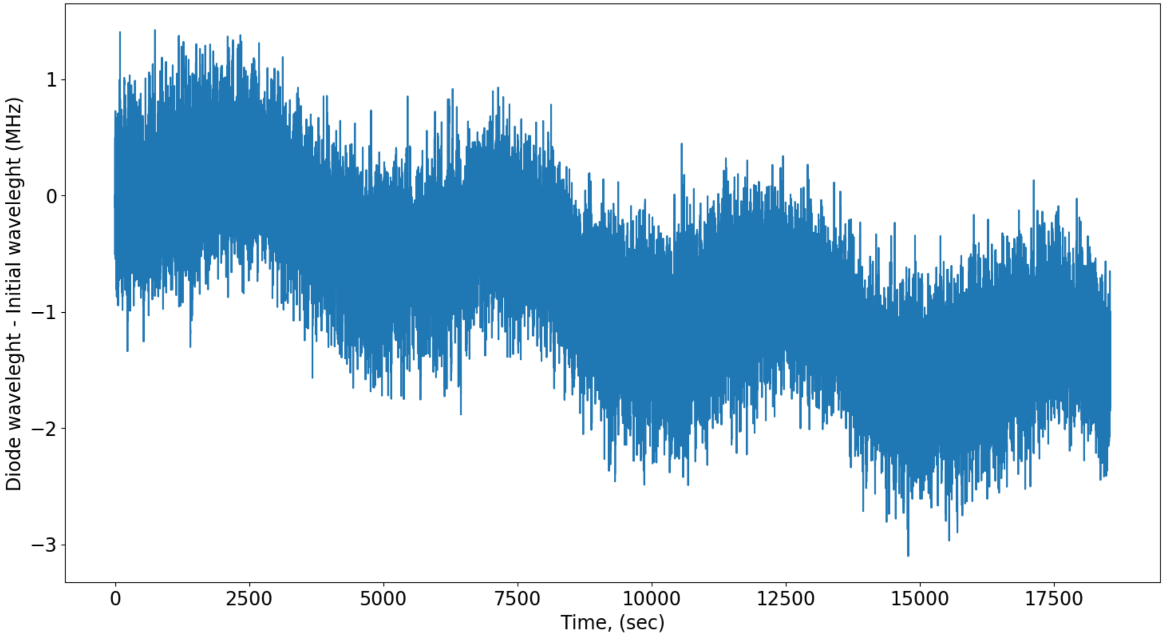
- The selected peaks on the Q-branch does not affect the retrieved molecular constants.
- The nuclear moments of ^{223}RaF has been extracted and are in close agreement with the atomic data.
- Determine the number of R-lines needed to extract nuclear moments with enough precision (work in progress).

Thank you for your attention

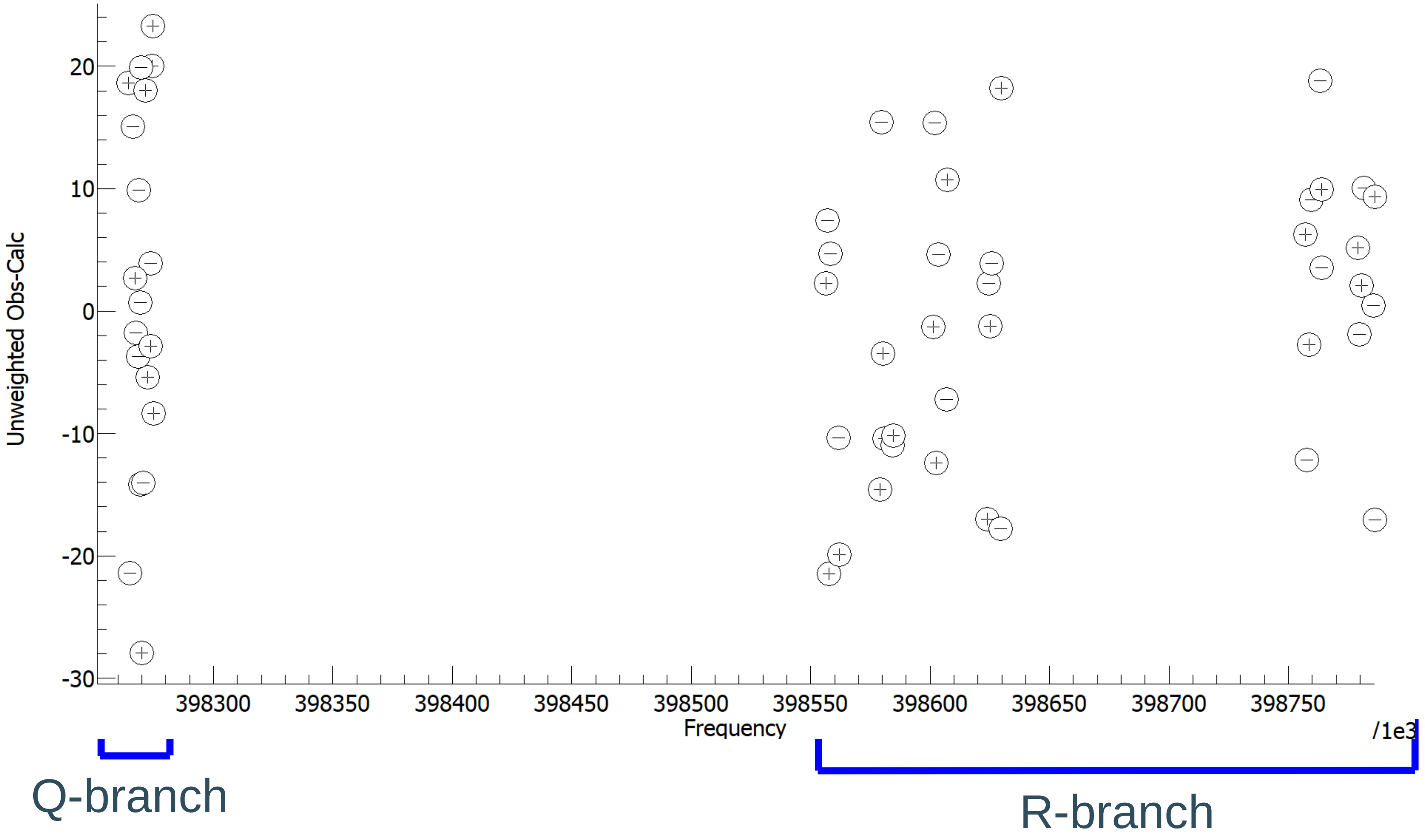
Backup slides

Scan 6145 variation of ISCOOL and diode (example)



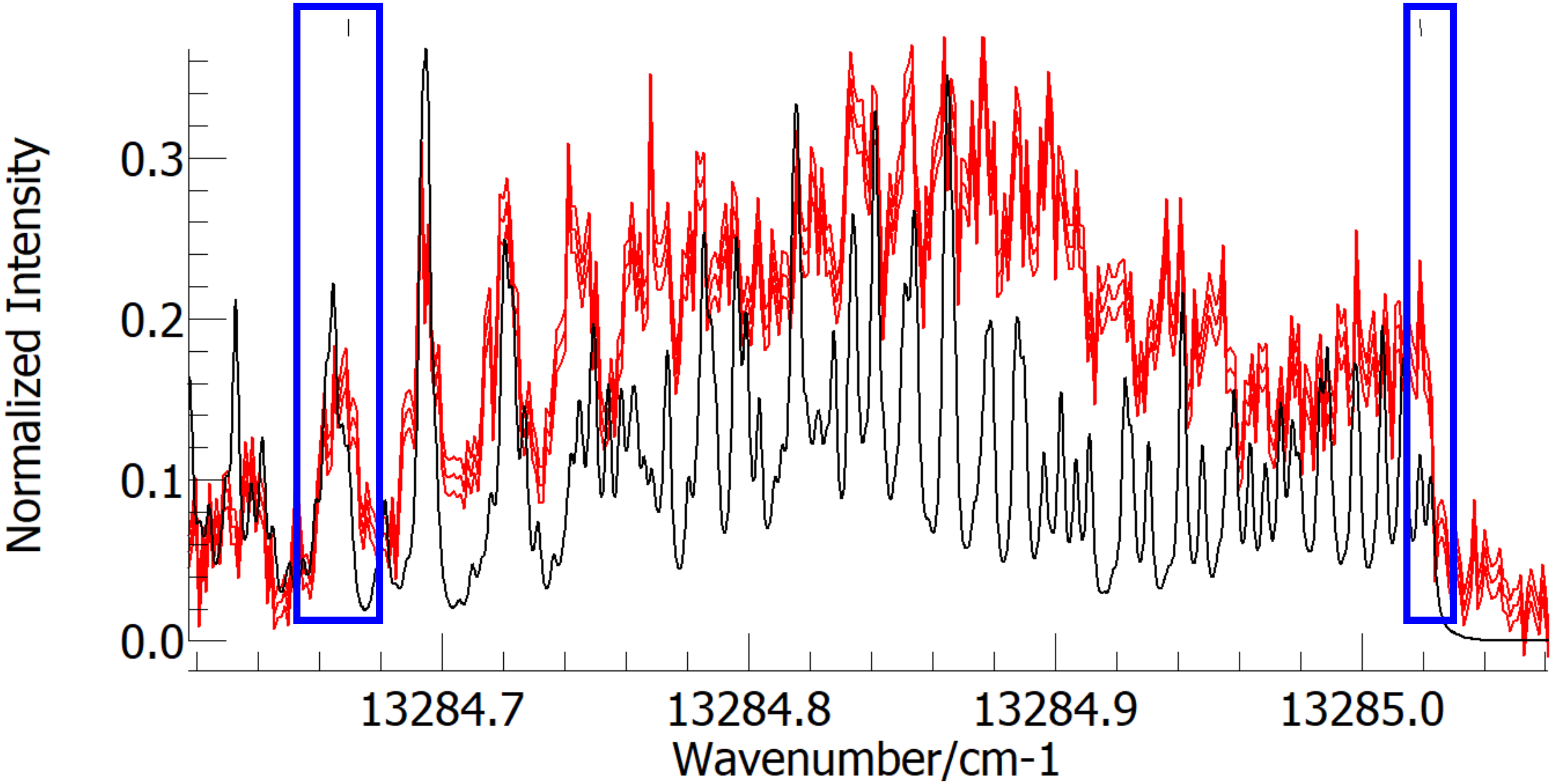


Residuals on the second fit (assigned lines)



Considerations for the second fitting

- The second fit starts by adding the farthest most peak on the spectrum.



Considerations for the second fitting

- The rotational constants must fall within the error bar of the scaled ones from ^{226}RaF and ^{225}RaF (not a constraint but a good check of the fit).
- The result from the second fit must match the band head of the Q-branch.
- This second fitting is with the intention to have a better idea for the assignments on the Q-branch.

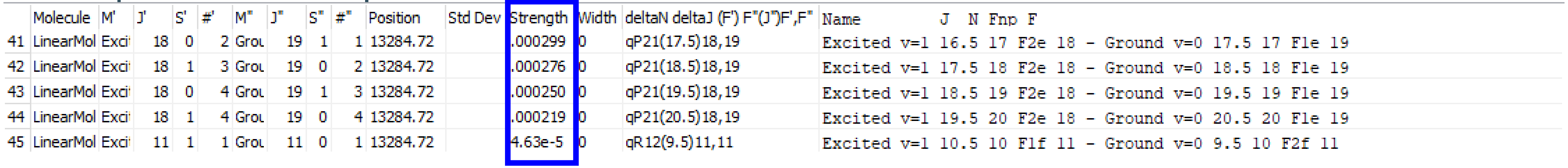
Note: The Q-branch was measured for low and medium J rotational lines. The latter rotational Q-branch was selected for the fit as it has **more resolved peaks**, a **narrower band head**, and the measured **R-branch** correspond to **medium rotational** lines (J = 11.5 to 21.5).

The selection of peaks

The peaks on the spectra can be made from different rotational transitions (lines), thus, when selecting a peak, the constrain can be impose over ill define rotational lines. Thus,

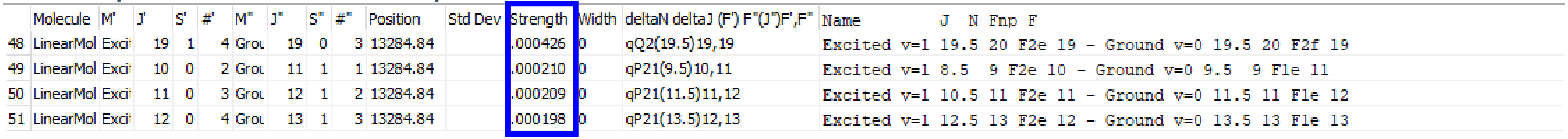
- Lines are added if the transition strength is clearly differentiated, or no other lines are present.

Example of ill define peak



	Molecule	M'	J'	S'	#'	M"	J"	S"	#"	Position	Std Dev	Strength	Width	deltaN deltaJ (F') F"(J")F',F"	Name J N Fnp F
41	LinearMol	Exci	18	0	2	Grou	19	1	1	13284.72		.000299	0	qP21(17.5)18,19	Excited v=1 16.5 17 F2e 18 - Ground v=0 17.5 17 F1e 19
42	LinearMol	Exci	18	1	3	Grou	19	0	2	13284.72		.000276	0	qP21(18.5)18,19	Excited v=1 17.5 18 F2e 18 - Ground v=0 18.5 18 F1e 19
43	LinearMol	Exci	18	0	4	Grou	19	1	3	13284.72		.000250	0	qP21(19.5)18,19	Excited v=1 18.5 19 F2e 18 - Ground v=0 19.5 19 F1e 19
44	LinearMol	Exci	18	1	4	Grou	19	0	4	13284.72		.000219	0	qP21(20.5)18,19	Excited v=1 19.5 20 F2e 18 - Ground v=0 20.5 20 F1e 19
45	LinearMol	Exci	11	1	1	Grou	11	0	1	13284.72		4.63e-5	0	qR12(9.5)11,11	Excited v=1 10.5 10 F1f 11 - Ground v=0 9.5 10 F2f 11

Example of a well define peak



	Molecule	M'	J'	S'	#'	M"	J"	S"	#"	Position	Std Dev	Strength	Width	deltaN deltaJ (F') F"(J")F',F"	Name J N Fnp F
48	LinearMol	Exci	19	1	4	Grou	19	0	3	13284.84		.000426	0	qQ2(19.5)19,19	Excited v=1 19.5 20 F2e 19 - Ground v=0 19.5 20 F2f 19
49	LinearMol	Exci	10	0	2	Grou	11	1	1	13284.84		.000210	0	qP21(9.5)10,11	Excited v=1 8.5 9 F2e 10 - Ground v=0 9.5 9 F1e 11
50	LinearMol	Exci	11	0	3	Grou	12	1	2	13284.84		.000209	0	qP21(11.5)11,12	Excited v=1 10.5 11 F2e 11 - Ground v=0 11.5 11 F1e 12
51	LinearMol	Exci	12	0	4	Grou	13	1	3	13284.84		.000198	0	qP21(13.5)12,13	Excited v=1 12.5 13 F2e 12 - Ground v=0 13.5 13 F1e 13

The selection of peaks

The peaks on the spectra can be made from different rotational transitions (lines), thus, when selecting a peak, the constrain can be impose over ill define rotational lines. Thus,

- Lines are added if the transition strength is clearly differentiated, or no other lines are present.
- The added peaks should be as separated as possible.
- After the addition of each peak, the spectrum is fitted, and the residuals are checked.

Linewidth determination

Rotational Line	FWHM (MHz). With Gauss = 15MHz	FWHM (MHz). With Gauss = 6MHz
1	61(11)	58(12)
2	119(18)	118(18)
3	87(11)	86(11)
4	102(10)	101(10)
5	71(7)	69(8)
6	68(7)	66(8)
Weighted mean	78(4)	77(4)

Constrains used:
-All the peaks share the same FWHM
-Gaussian contribution tended to go to $3e^{-3}$ MHZ. Thus, constrained to 15 MHz assuming an energy spread on the bunch of 4eV. However, lower values do not change the linewidths.

Peak position + 13294 (arb offset) cm-1

Peak	J11.5	J12.5	J13.5	J14.5	J20.5	J21.5
1	0.4102(2)	1.1607(4)	1.9113(2)	2.6587(3)	7.1028(2)	7.8360(2)
2	0.4306(4)	1.1832(5)	1.9340(3)	2.6819(3)	7.1284(1)	7.8626(2)
3	0.4497(3)	1.2039(6)	1.9578(3)	2.7041(4)	7.1542(1)	7.8886(2)
4	0.4712(2)	1.2264(7)	1.9782(3)	2.7283(4)	7.1835(2)	7.9182(2)
5	0.5865(3)	1.3415(7)	2.0948(3)	2.8415(2)	7.3147(3)	8.0524(2)
6	0.5975(2)	1.3546(3)	2.1091(2)	2.8615(2)	7.3331(2)	8.0713(4)
7	-	-	-	-	7.3377(3)	8.0758(5)
χ^2_{red}	2.79	2.97	2.98	3.61	4.18	3.08

The retrieved centroids were taken to PGOPGER for the initial fit keeping the rotational contribution constants.

The error on the peaks center ranges between ~3 and ~21 MHz.

Molecular constants with Q lines (mean)

Constant	1 line	3 lines	6 lines	9 lines	12 lines	15 lines	18 lines
B''	5761.67(100)	5761.59(8)	5761.48(4)	5761.51(4)	5761.56(3)	5761.54(3)	5761.56(3)
b	2036(70)	2034(5)	2031(3)	2029(2)	2029(2)	2030(2)	2029(2)
c	36(141)	41(12)	48(7)	51(7)	53(7)	51(7)	53(7)
eqQ	-1525(252)	-1513(38)	-1494(29)	-1487(28)	-1479(27)	-1477(26)	-1473(25)
T	13284.6971(9)	13284.6972(1)	13284.6974(1)	13284.6974(1)	13284.6974(1)	13284.6975(1)	13284.6974(1)
B'	5732.08(90)	5732.00(8)	5731.90(4)	5731.93(3)	5731.96(3)	5731.95(3)	5731.96(3)
d	244(64)	246(5)	250(2)	251(2)	252(2)	251(2)	252(2)
eqQ	-981(267)	-969(31)	-952(23)	-948(21)	-940(21)	-943(21)	-939(20)

Using all 19 lines

B''	5761.56(3)
b	2029(2)
c	53(7)
eqQ	-1472(25)

T	13284.6975(1)
B'	5731.96(3)
d	252(2)
eqQ	-939(21)

Doppler contribution to linewidth

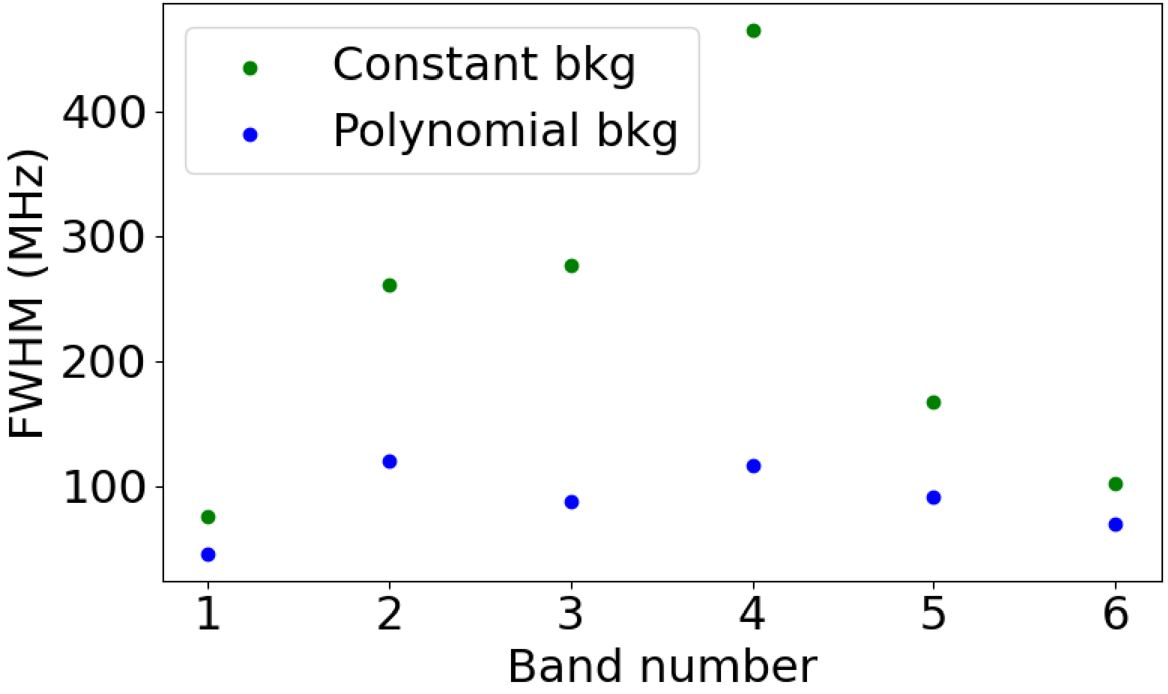
$$\delta \nu_D = \nu_0 \frac{\delta E}{c\sqrt{2eV_{acc}m}}$$

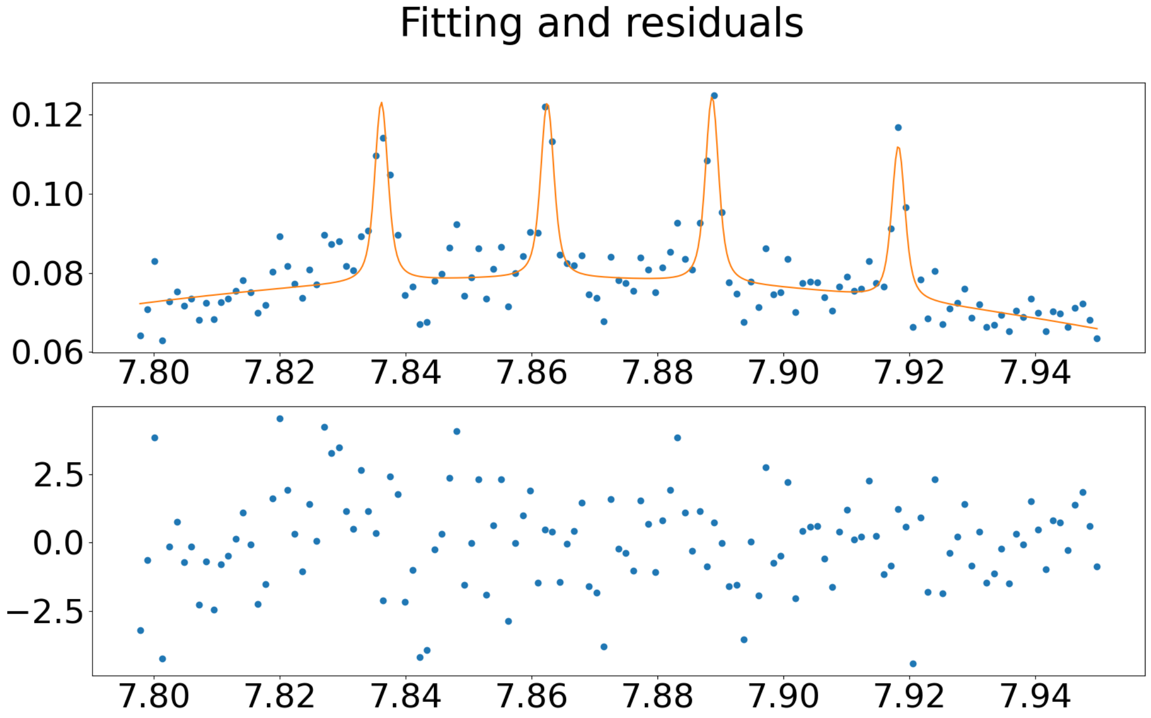
δE = it’s the kinetic energy spread (4eV)
e = is the elemental charge (1.6e-19 C)
m = mass of the molecule (223+19 in eV)
V_{acc} = acceleration voltage (30keV)
C = speed of light (m/s)
ν_0 = centroid frequency 13284.695 (cm-1)

→

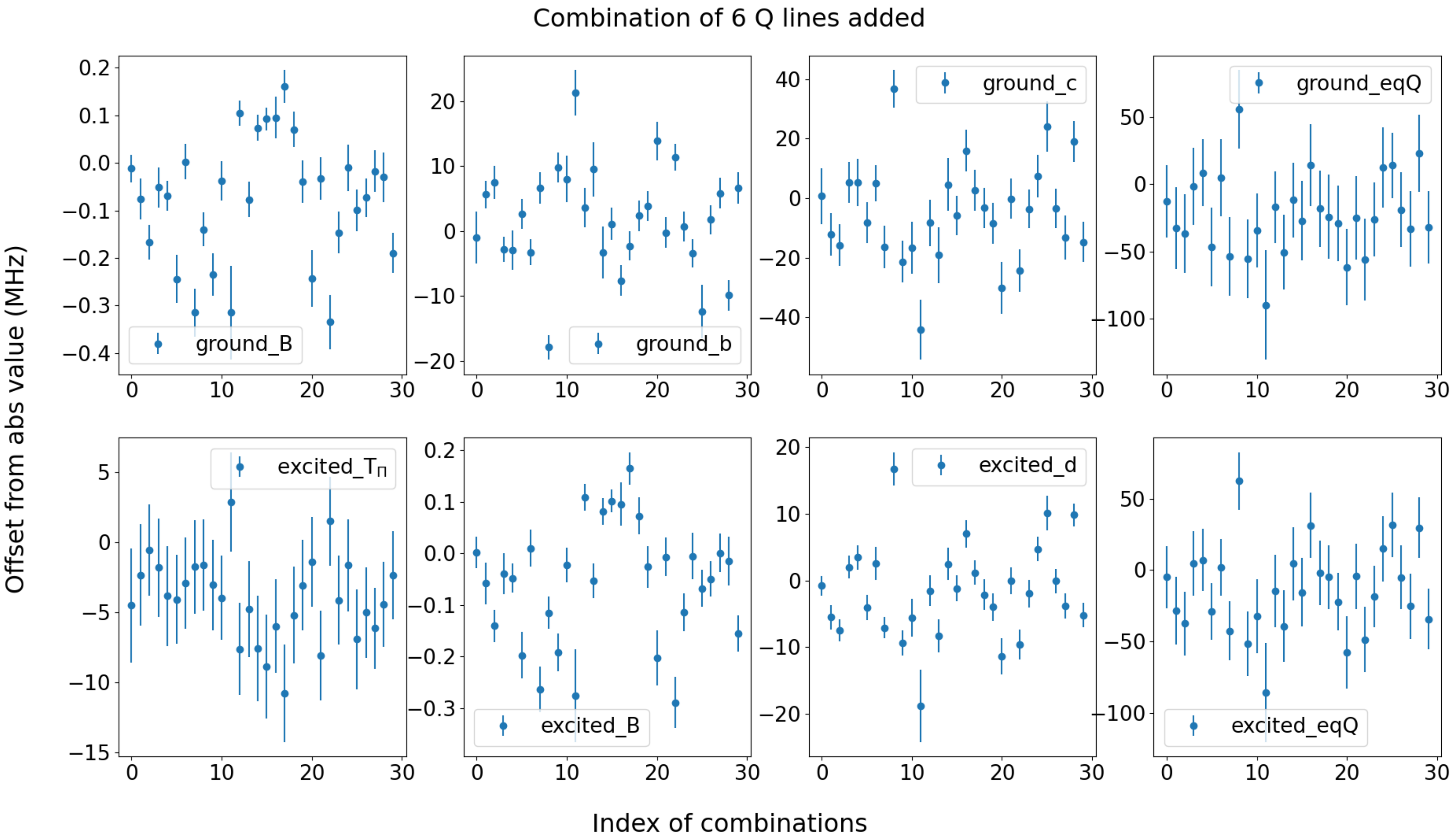
Gaussian contribution = 14 MHz for 4eV
Gaussian contribution = 7 MHz for 2eV

Polynomial background and residuals





Molecular constants with 6 Q lines (statistical errors)

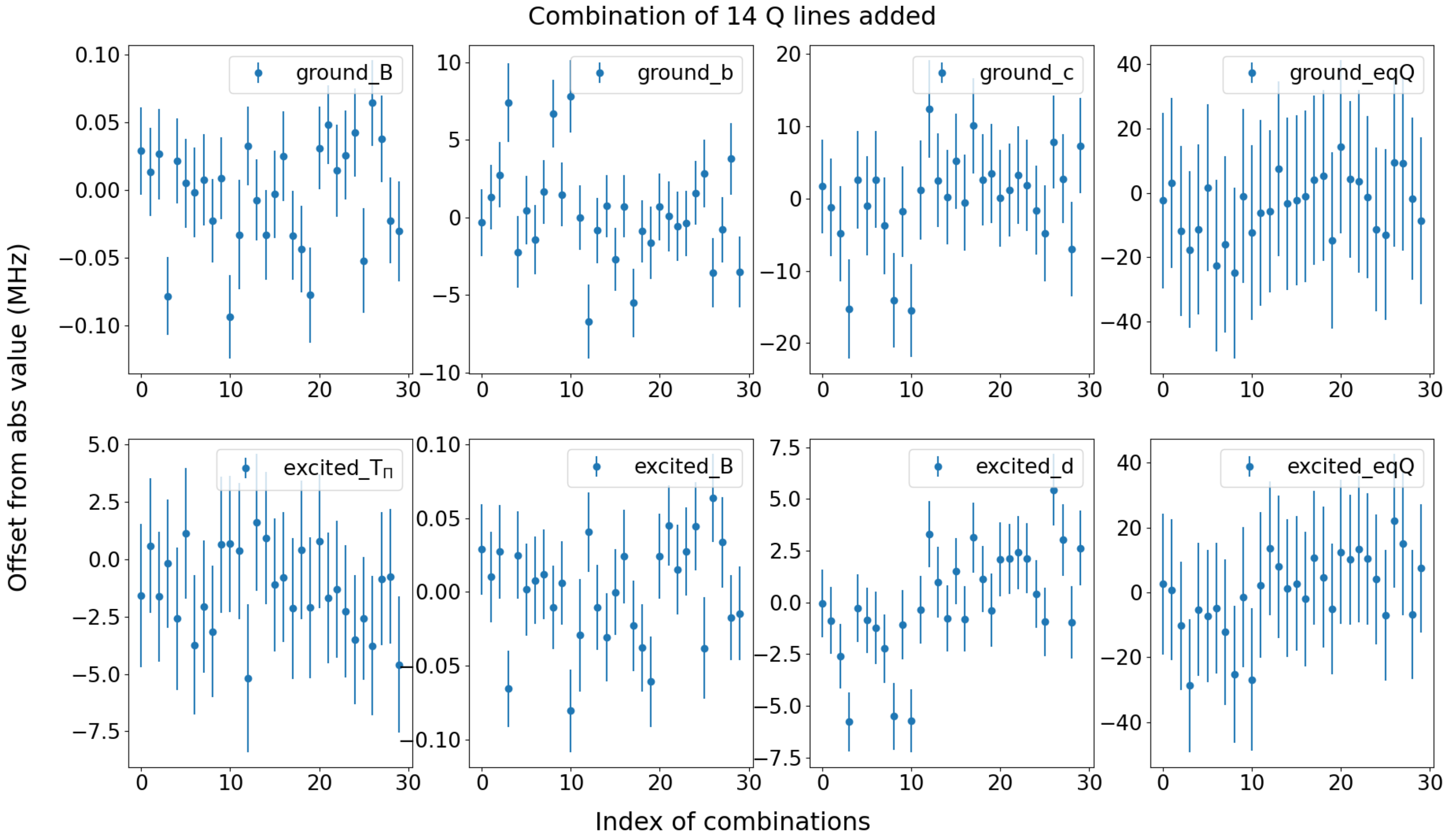


Reported nuclear moments ^{223}Ra

Method	Year	μ	Q_s	Transition	Ref
CLS	1983	0.280(14)	1.20(20)	$7s^2\ {}^1S_0 - 7s7p\ 1P_1$ $*\ 7s^2\ {}^2S_{1/2} - 7s7p\ 2P_{1/2}$	Determination of nuclear spins and moments in a series of radium isotopes. *Physics Letters B*, *133*(1-2), 47-52.
CLS	1987	0.267(14) *0.260(13)	1.20(6) -	$7s^2\ {}^1S_0 - 7s7p\ 1P_1$ $*\ 7s^2\ {}^2S_{1/2} - 7s7p\ 2P_{1/2}$	On the hyperfine structure and isotope shift of radium. *Zeitschrift für Physik D Atoms, Molecules and Clusters*, *4*, 227-241.
CLS+LP	1987	**0.2705(19)**	-	$7s^2\ {}^1S_0 - 7s7p\ 1P_1$	Direct measurement of nuclear magnetic moments of radium isotopes. *Physical Review Letters*, *59*(7), 771.
CLS	1988	0.2705(19)	1.19(12)	$7s^2\ {}^1S_0 - 7s7p\ 1P_1$	Mean square charge radii of radium isotopes and octupole deformation in the 220–228Ra region. *Nuclear Physics A*, *483*(2), 244-268.
CLS	1989	*0.271(3)	*1.19(13)	$*\ 7s^2\ {}^2S_{1/2} - 7s7p\ 2P_{1/2}$ $*\ 7s^2\ {}^2S_{1/2} - 7s7p\ 2P_{3/2}$	Quadrupole moments of radium isotopes from the 7 p 2 P 3/2 hyperfine structure in Ra II. *Zeitschrift für Physik D Atoms, Molecules and Clusters*, *11*, 105-111.
Theory (EFG)	2005	-	1.218 1.194 1.211	$7s^2\ {}^1S_0 - 7s7p\ 1P_1$ $7s^2\ {}^1S_0 - 7s7p\ 3P_1$ $7s^2\ {}^1S_0 - 7s7p\ 3P_2$	Degree of accuracy in determining the nuclear electric quadrupole moment of radium
CRIS	2018	0.2703(6)	1.259(67)	$7s^2\ {}^1S_0 - 7s7p\ 3P_1$	Laser-spectroscopy studies of the nuclear structure of neutron-rich radium. *Physical Review C*, *97*(2), 024309.

- Measured in Ra+
- LP: Larmor precession

Molecular constants with 14 Q lines (statistical errors)



Fitting of the ^{223}RaF saturated spectra.

Parameter	Non saturated	Saturated (+11 peaks)
B”	5761.560(30)[7]	5761.570(40)
b	2029.0(20)[5]	2028.0(30)
c	53(7)[2]	53(9)
eqQ	-1472(25)[5]	-1447(26)
T	13284.69750(10)[2]	13284.69750(10)
B’	5731.960(30)[7]	5731.970(30)
d	251.5(20)[3]	251.3(20)
eqQ	-939(21)[4]	-918(22)

$Q(^{223}\text{RaF})_{\text{ground}}$ = 1.21(7) b
$Q(^{223}\text{RaF})_{\text{excited}}$ = 1.25(7) b

$Q(^{223}\text{RaF})_{\text{ground}}$ = 1.19(7) b
$Q(^{223}\text{RaF})_{\text{excited}}$ = 1.22(7) b

$Q(^{223}\text{Ra})_{\text{ground}}$ = 1.21(7) b

Background present on the spectra

The line strength of a molecular dipole transition between HFS states is proportional to,

$$\left\langle \mathrm{N'SJ'IF'} \left| \mu^{(1)} \right| \mathrm{NSJIF} \right\rangle$$

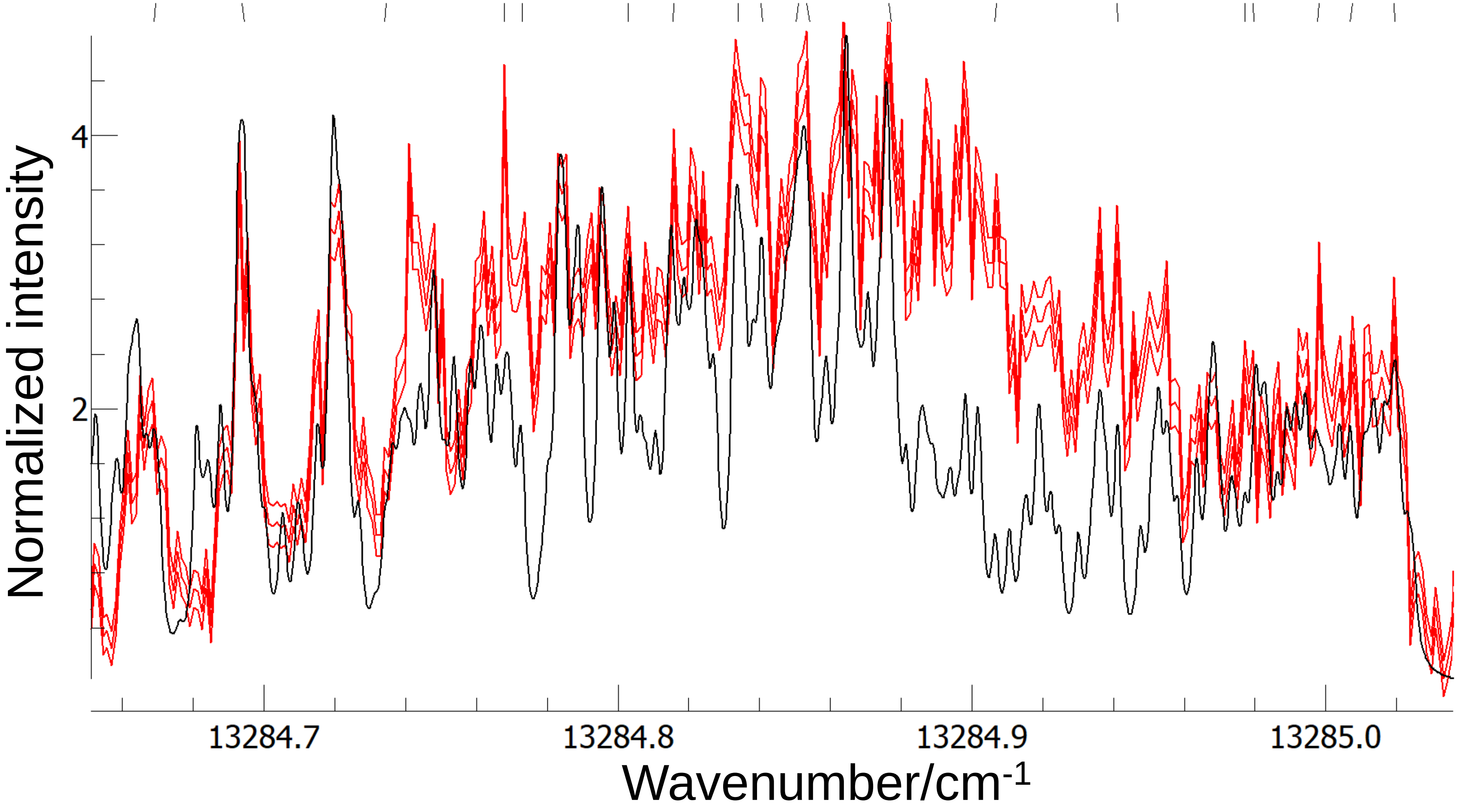
$$\propto \left[(2\ \mathrm{J}+1)\,(2\ \mathrm{J'}+1)\,(2\ \mathrm{F}+1)\,(2\ \mathrm{F'}+1) \right]^{1/2} \left\{ \begin{array}{ccc} \mathrm{N'} & \mathrm{J'} & \mathrm{S} \\ \mathrm{J} & \mathrm{N} & 1 \end{array} \right\} \left\{ \begin{array}{ccc} \mathrm{J'} & \mathrm{F'} & \mathrm{I} \\ \mathrm{F} & \mathrm{J} & 1 \end{array} \right\}$$

Where the terms in {} is the Wigner 6j symbols. For a transition between…(R-branch) the intensity of a $\Delta F = +1$ is ~18 and ~666 times stronger than a $\Delta F = 0$ and a $\Delta F = -1$ transition, respectively.

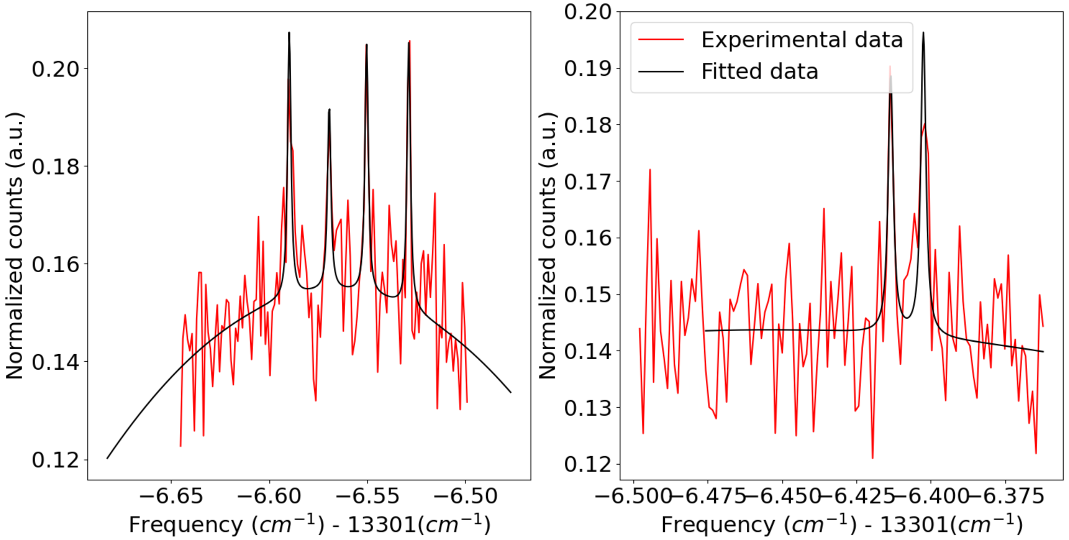
If the transition energies the $\Delta F = 0$ are calculated (based on the final fit), the position of the peaks are mainly within the quadruplet observed.

[2] Campbell, W. C. (2008), Doctoral dissertation, Harvard University.
[3] Breier, A. A. (2019). Doctoral dissertation, kassel university press GmbH.

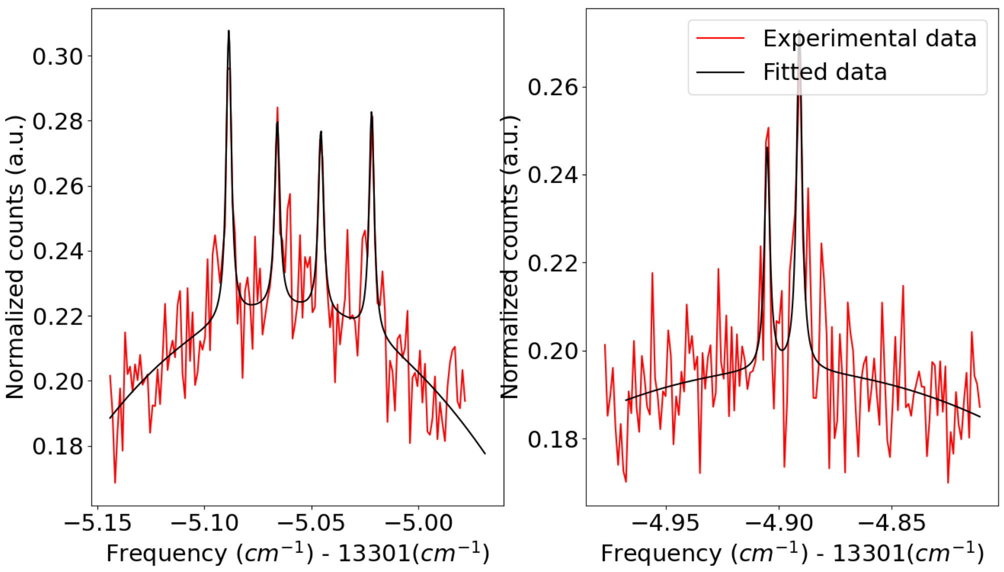
Final Q-branch result



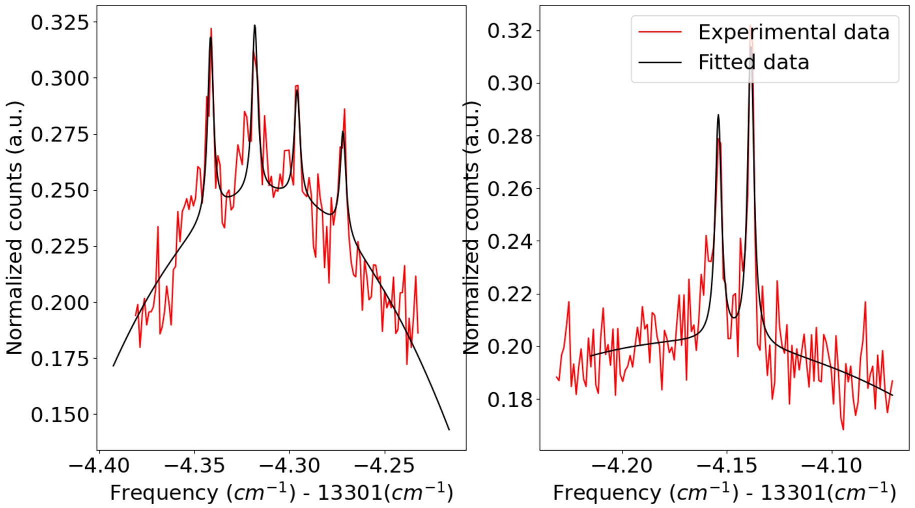
First rotational line



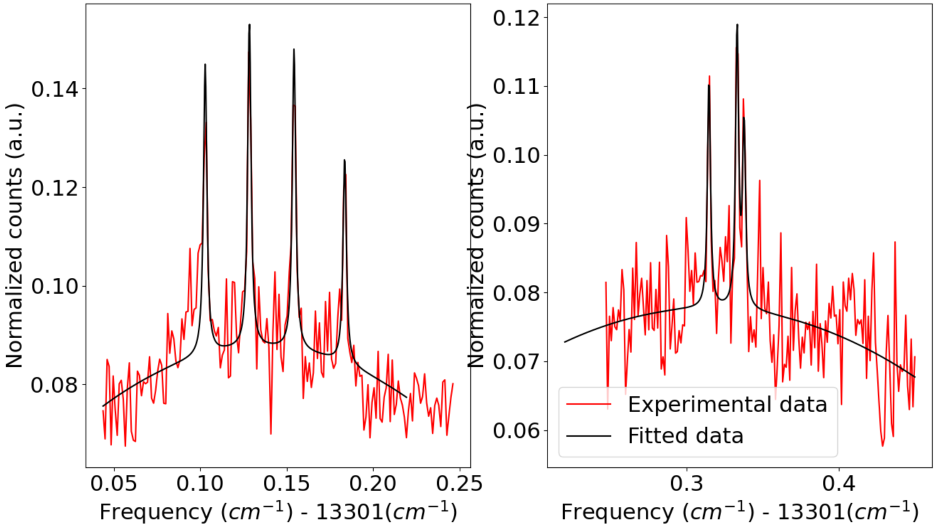
Third rotational line



Forth rotational line



Fifth rotational line



Molecular constants with different number of R lines