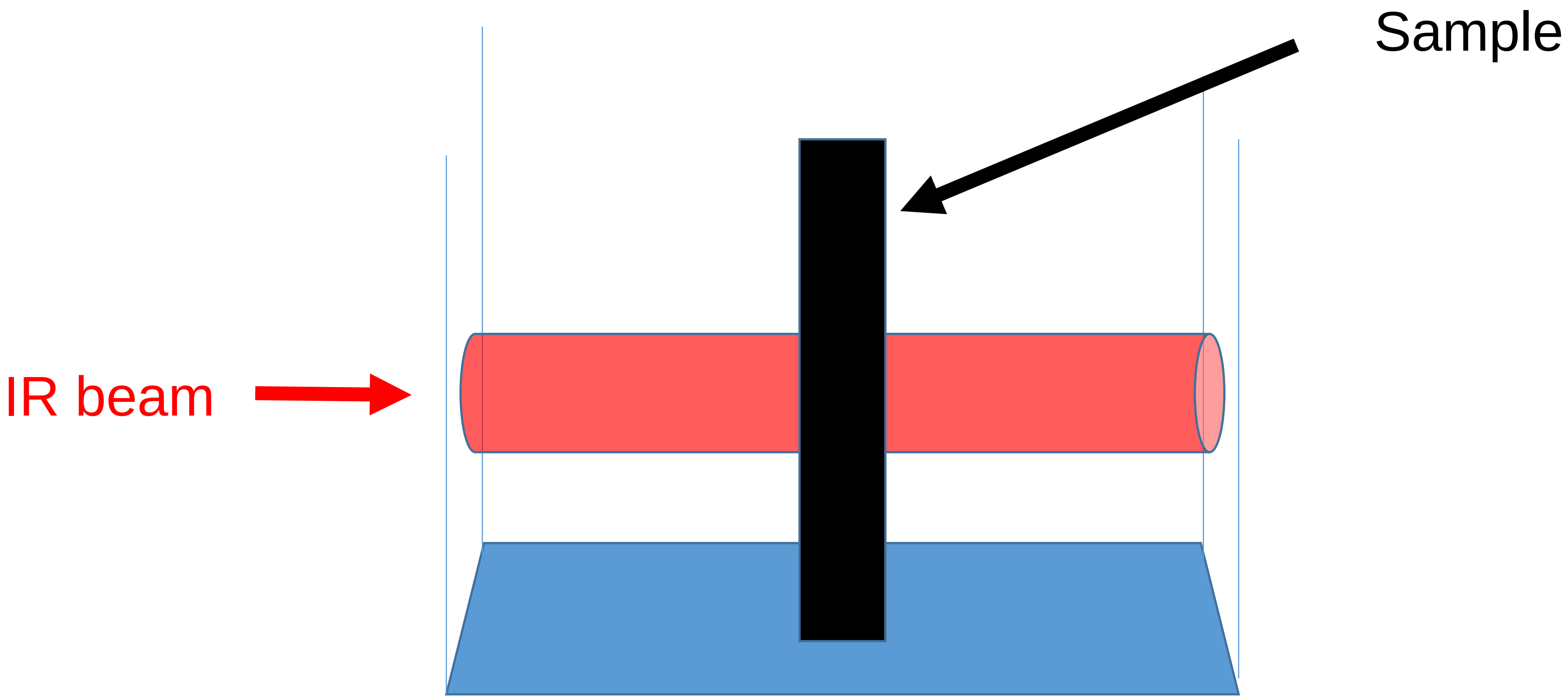
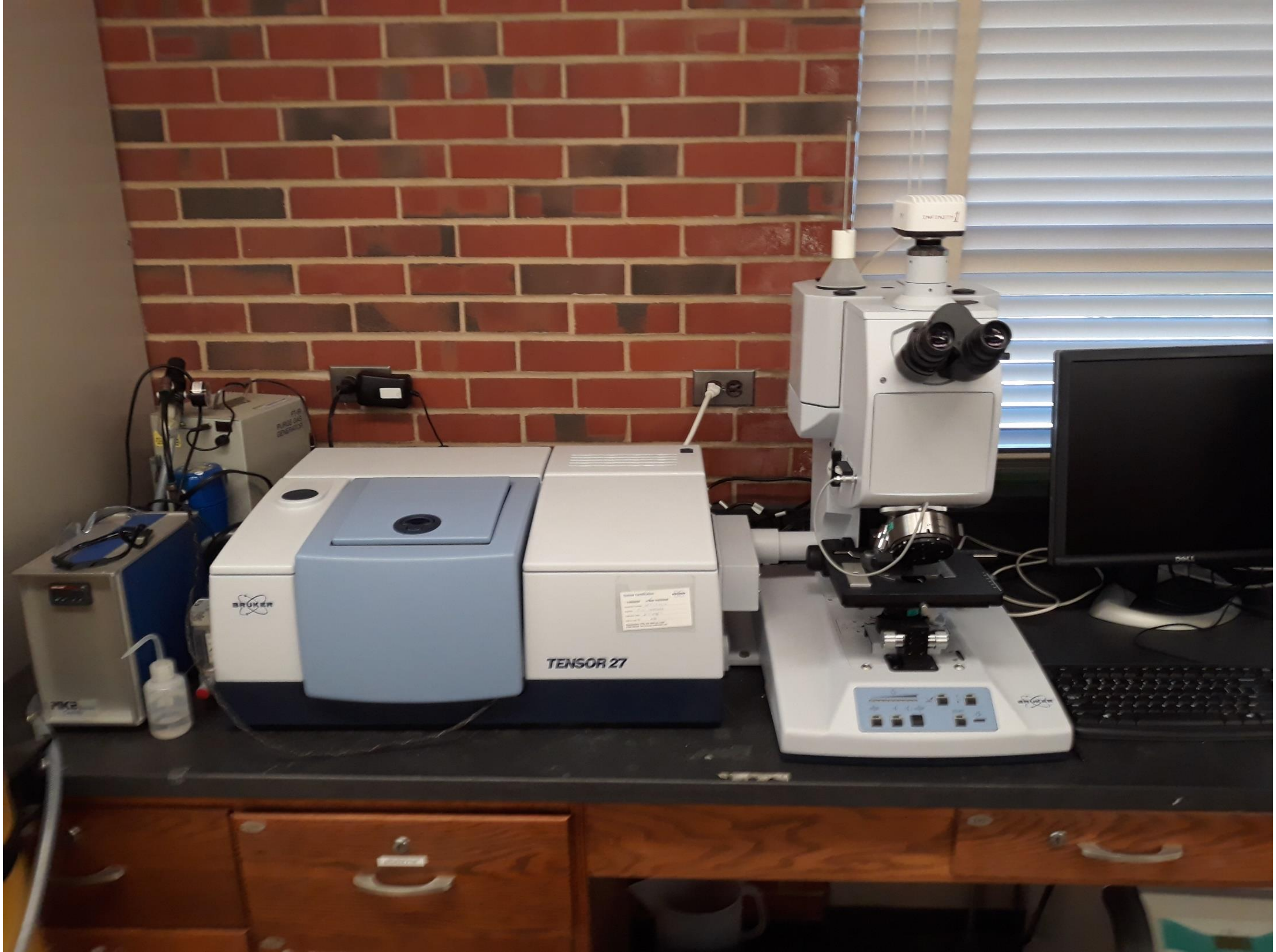
Fourier transform infrared measurement of the HCl spectrum

Our experiment: rovibrational levels of HCl

The FTIR bench is a versatile platform with several different types of attachments For detection of ATR, IRRAS, transmission and microscopy. We are using a Bruker Tensor 22 FTIR. The second slide shows the sample compartment. The beam passes through the middle of the sample chamber




BRUKER
TENSOR 27

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PURGE GAS
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PIKE

Our experiment: rovibrational levels of HCl

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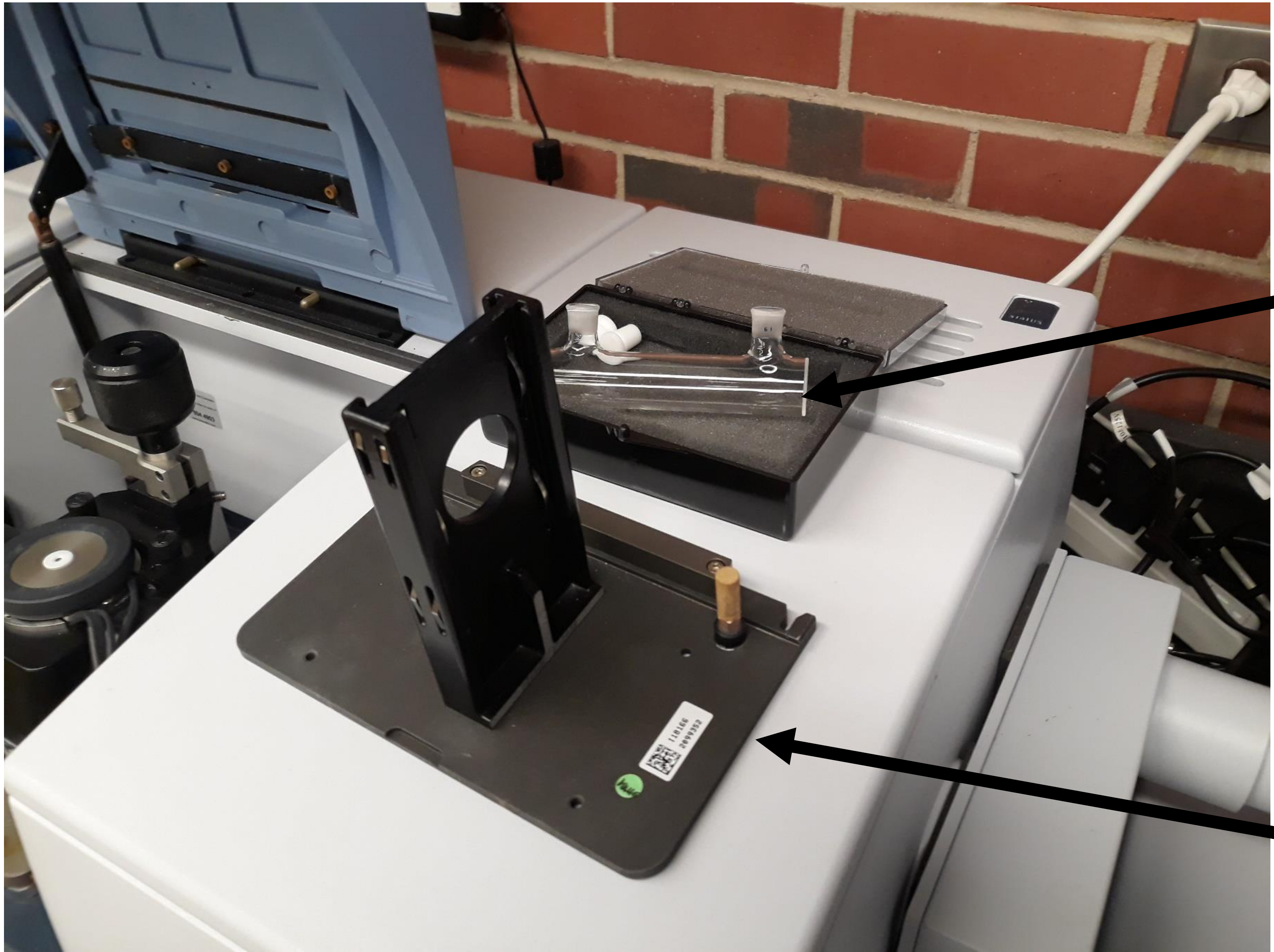
For detection of ATR, IRRAS, transmission and microscopy.

We use a 10 cm quartz cuvette. Why quartz? What materials are used for FTIR? What do they cost? Do a little web search to answer this question (with any example that you find reasonable).

Transmission sample holder and quartz sample cell



Cuvette

Sample Holder

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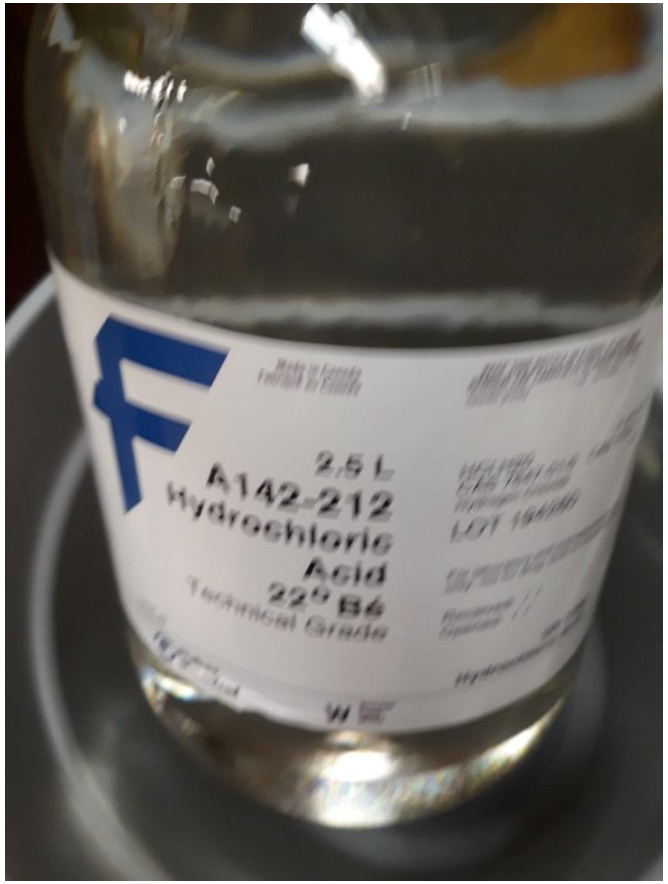
Quartz is much cheaper than other materials such as calcium fluoride or zinc
selenide. It absorbs very strongly near 1100 cm^{-1} due to the –Si-O-Si- modes. Even
The windows of the cell absorb 100% of the light below 2200 cm^{-1}. We can use
This cuvette only because HCl absorbs at ca. 2900 cm^{-1}.

Add concentrated HCl to the cuvette using a glass pipette. How can we detect HCl?

Prepare HCl sample using concentrated acid



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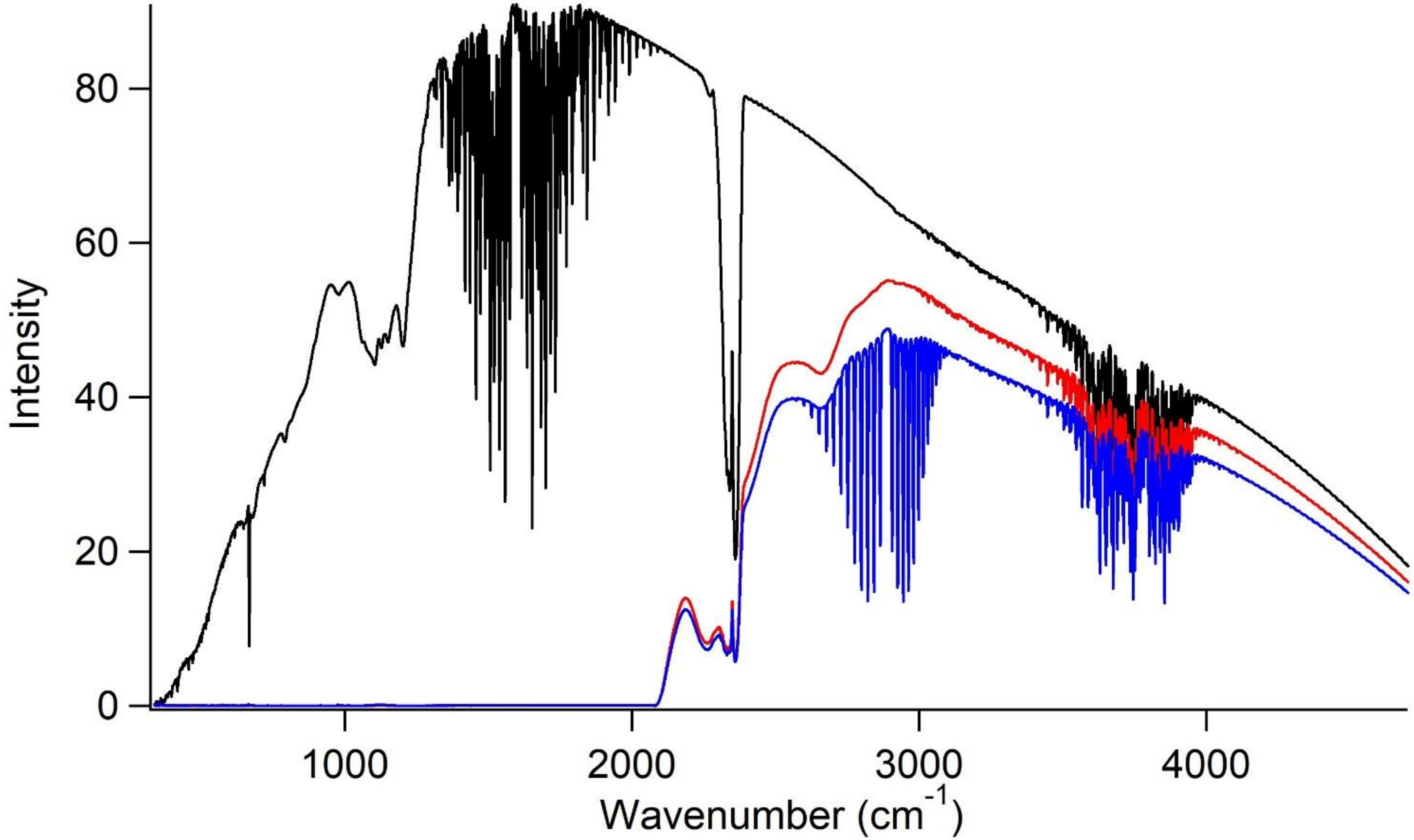
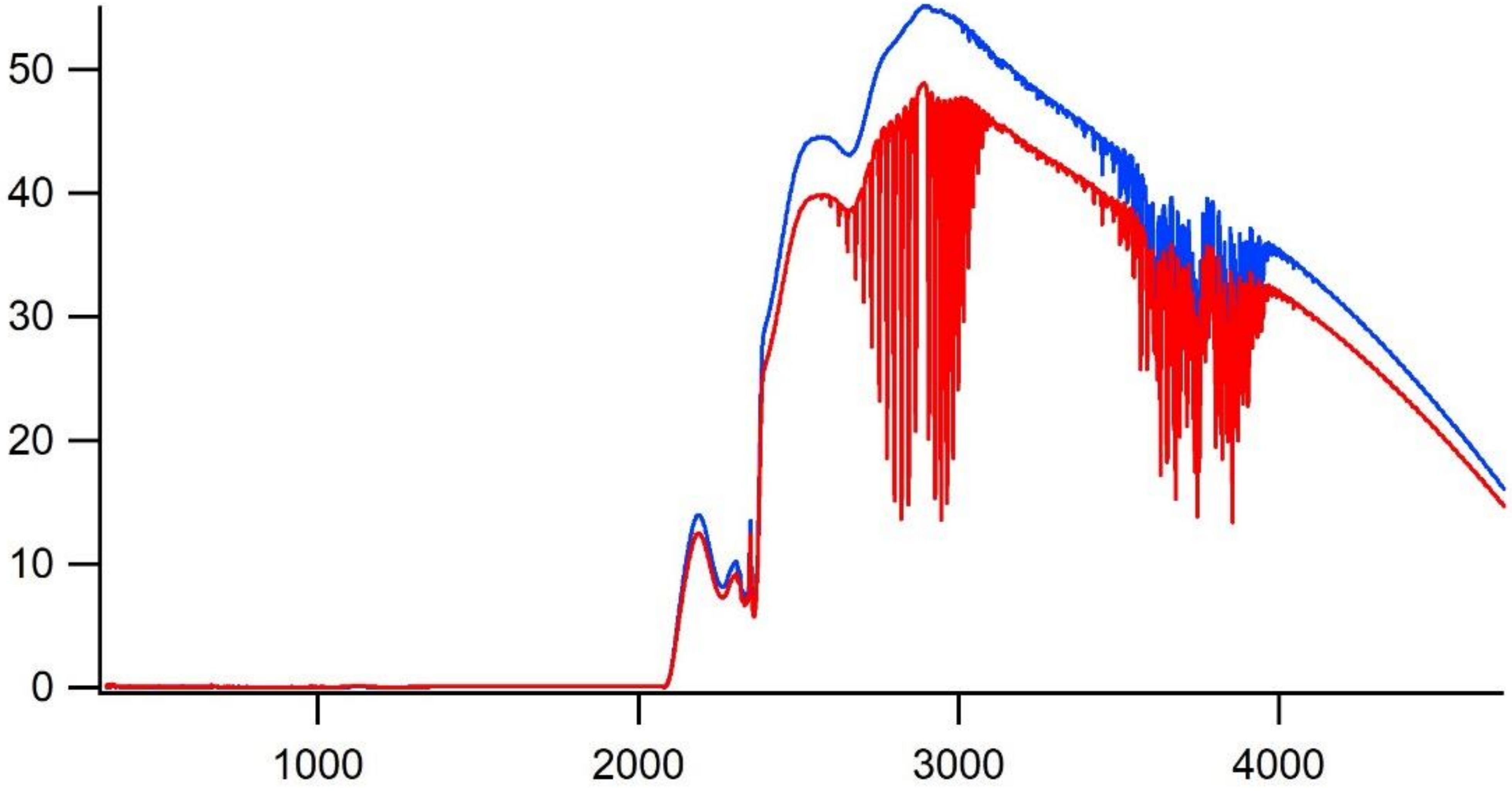
Add concentrated HCl to the cuvette using a glass pipette. How can we detect HCl?

Concentrated HCl has a very high vapor pressure. In a closed cell it vaporizes and fills the cell with enough HCl to easily detect the rovibrational bands.

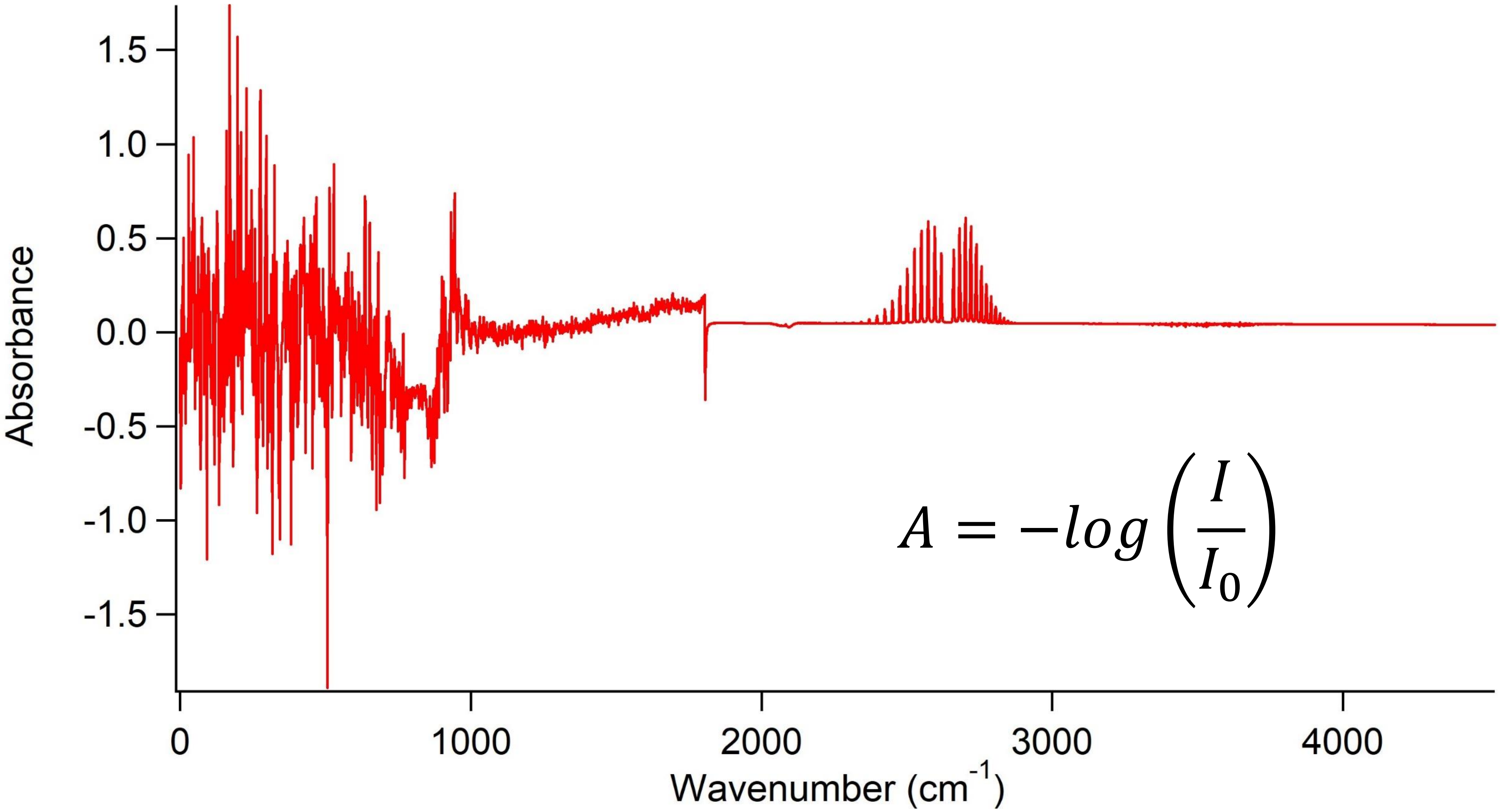
Background, silica and HCl



Focus on silica and HCl to obtain absorption spectrum

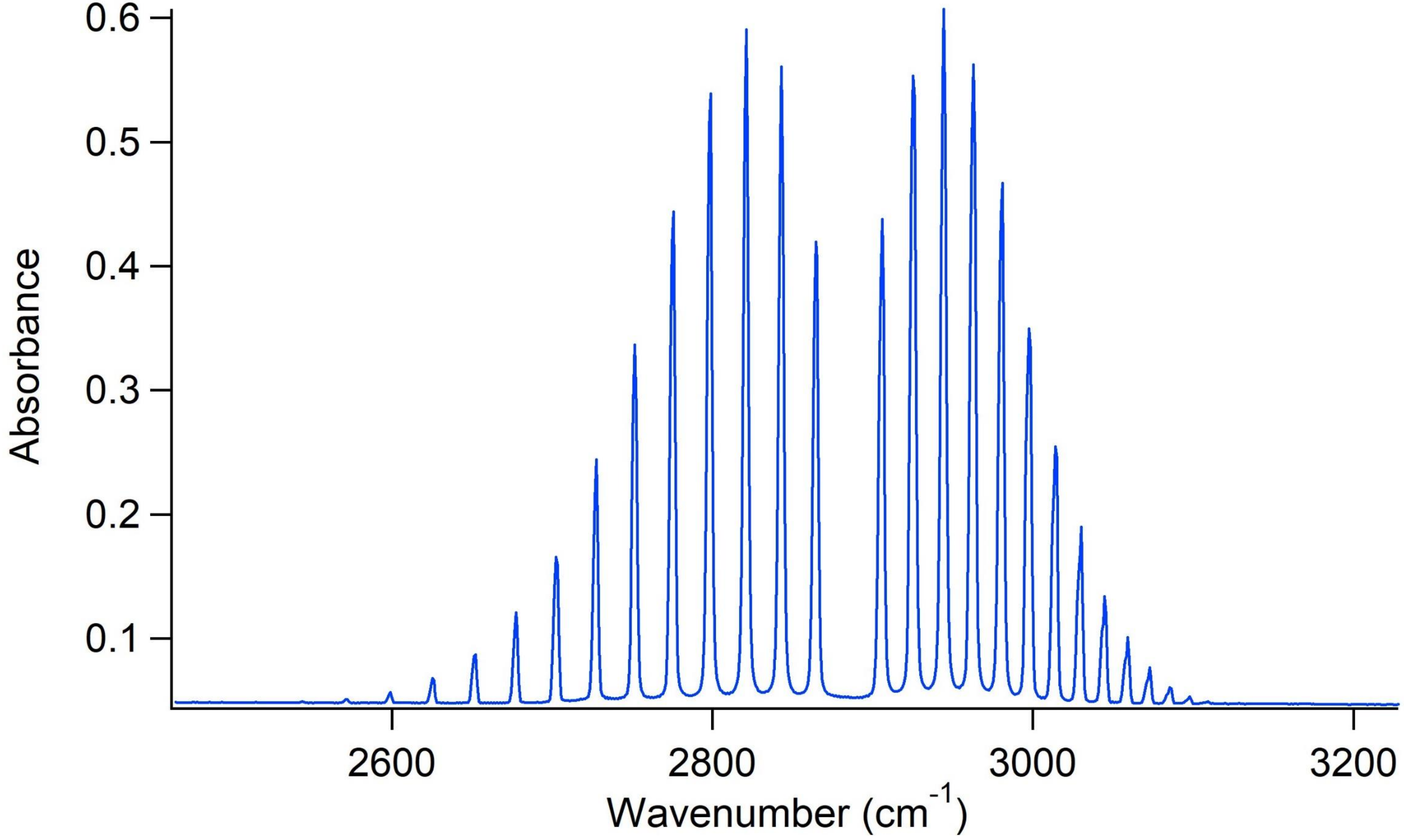


Absorbance of HCl sample

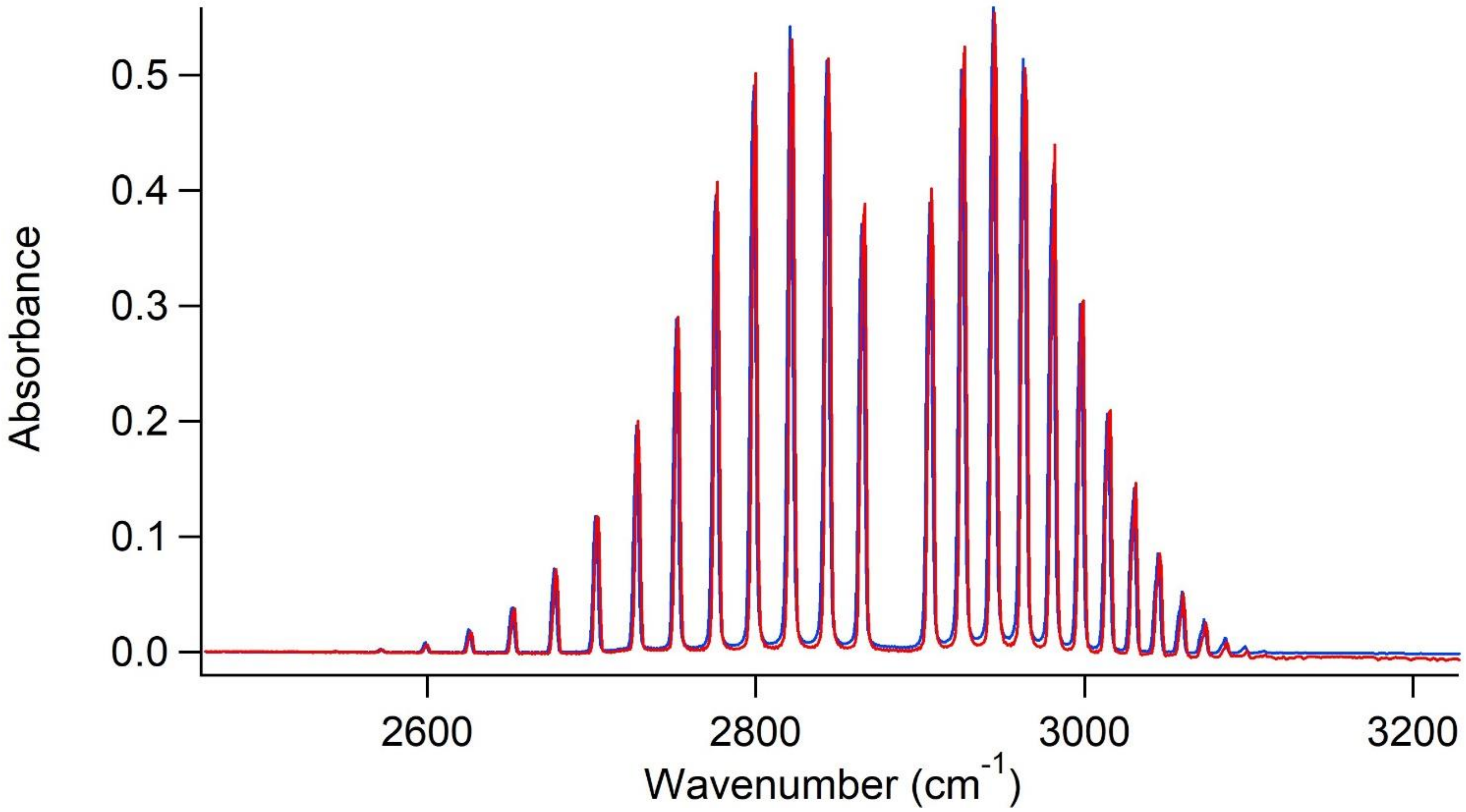


$$A = -log\left(\frac{I}{I_0}\right)$$

Absorbance of HCl sample



Comparison of absorbance of two HCl samples



The raw data obtained from the baseline corrected spectrum shown in the Figure

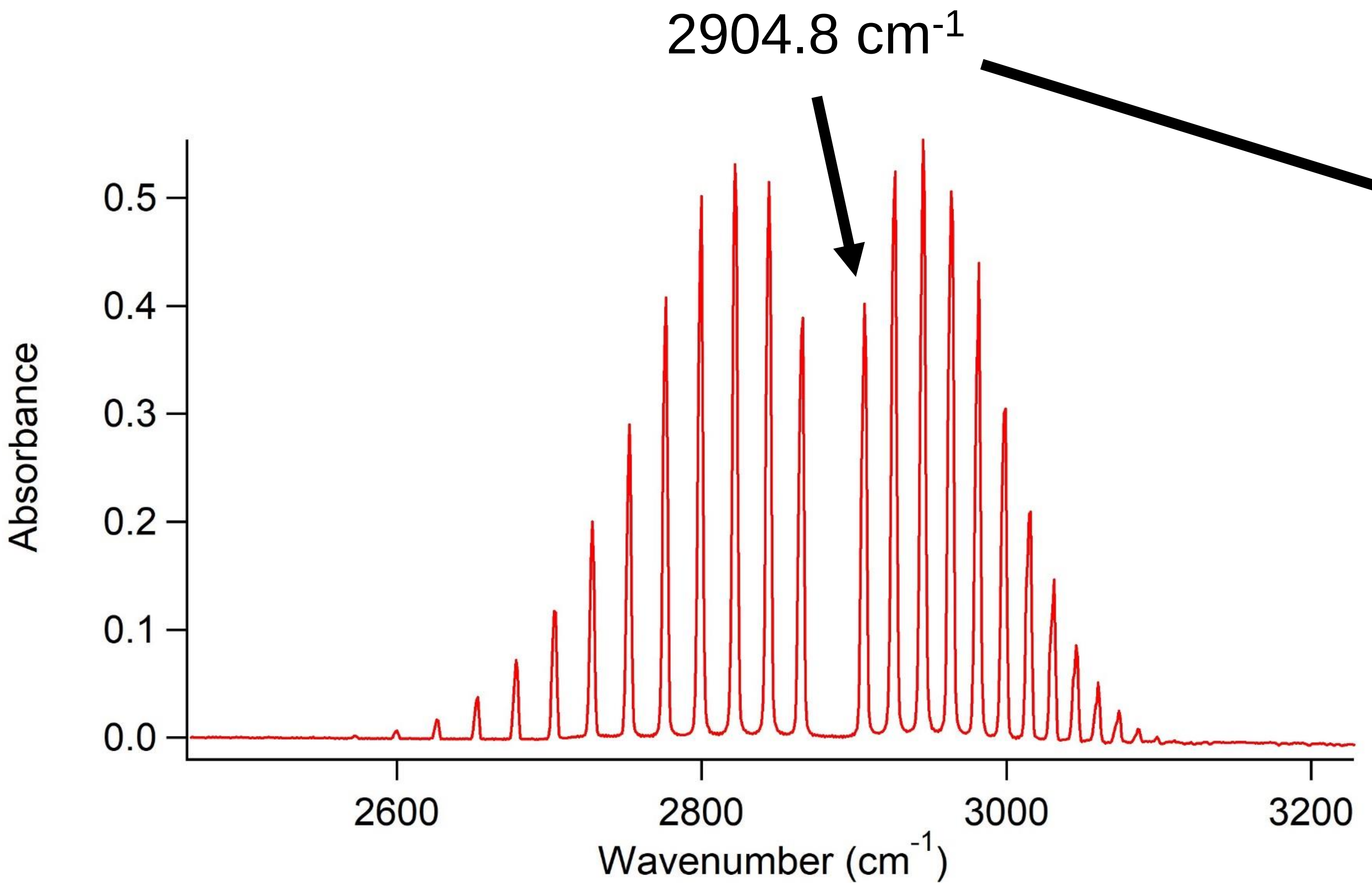
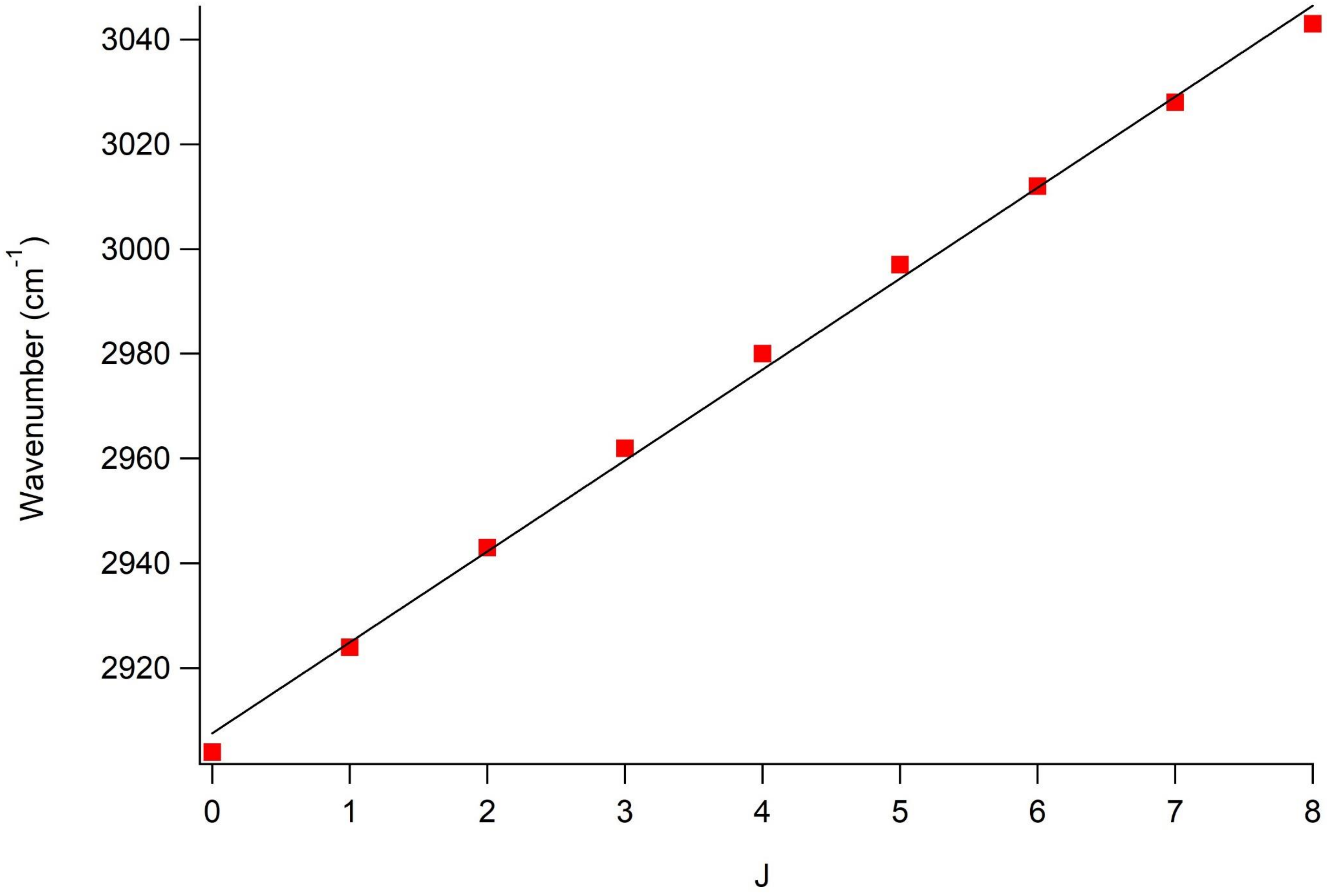


Table 1. Peak values of the R branch in cm^{-1}

0	2904.8
1	
2	
3	
4	
5	
6	
7	
8	

$$\tilde{\nu}_{obs} = \tilde{\nu}_o + 2(B_e - \alpha)m - \alpha m^2$$

Linear fit of HCl rovibrational spectra



These data were fit using linear least squares. Using the values in wavenumbers we fit the linear function,

$$\tilde{\nu} = a_0 + a_1 m + a_2 m^2$$

Where

$$a_0 = \tilde{\nu}_0$$

And

$$a_1 = 2\tilde{B} - 2\alpha$$

$$a_2 = -\alpha$$

The fit parameters are:

n	0	1
a_n	17.36	2908.00
σ_n	0.3258	1.5515

From these fit parameters we can obtain the Q brand wave number $\tilde{\nu}_0$ and the rotational constant $\tilde{B}$ cm^{-1}.

Centrifugal Distortion

Centrifugal distortion arises from the changing bond length of the molecule during rotation. Clear the rigid rotator approximation is not applicable to a read molecule and the chemical bond acts like a spring that alters the distance between the nuclei. The moment of inertia increases with the bond length squared and therefore the rotational constant decreases as the bond length increases. We can express this phenomenon as a correction to the rotational energy.

$$F(J) = BJ(J+1) - DJ^2(J+1)^2$$

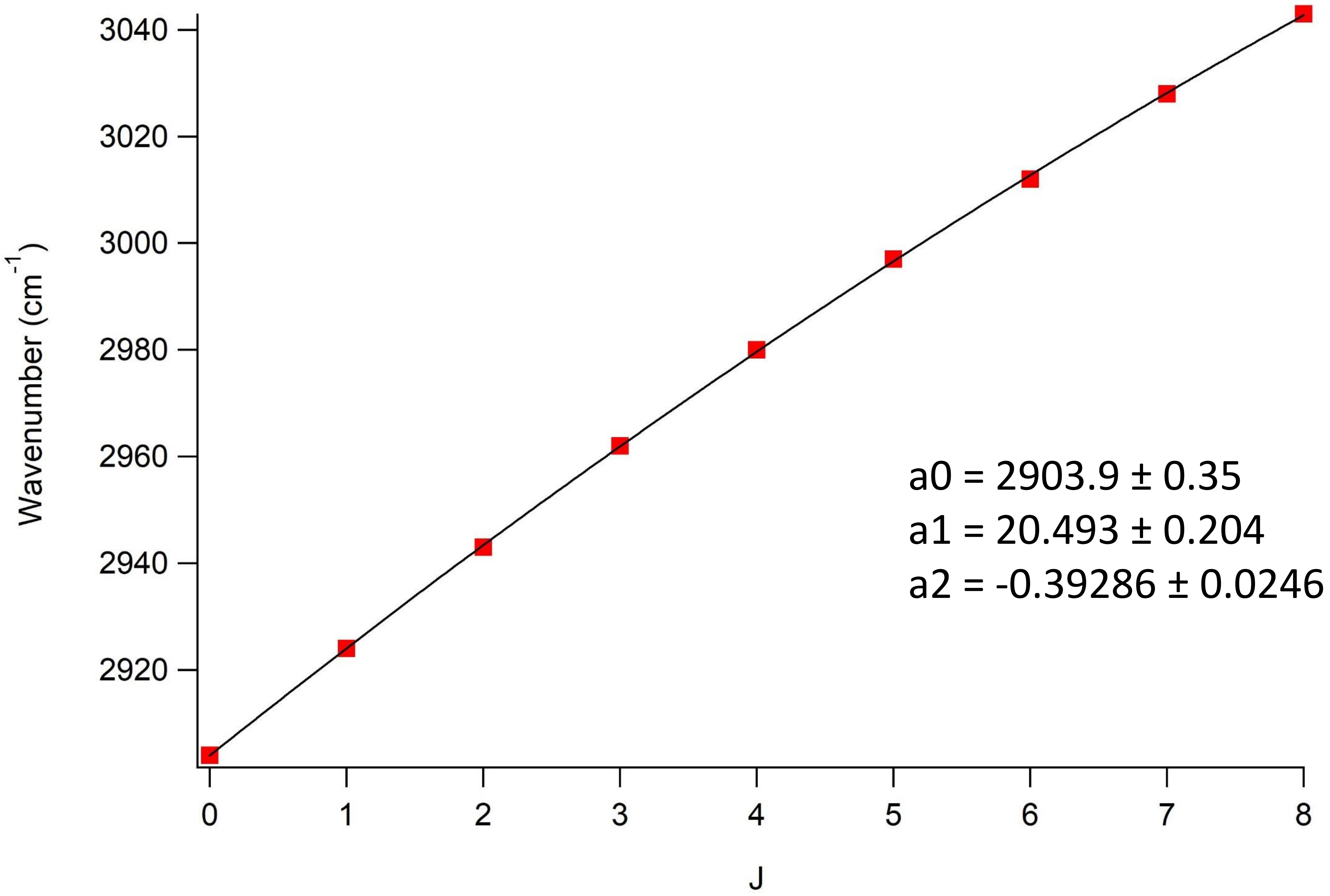
where D is the centrifugal distortion constant. D is related to the vibrational wavenumber,

Theoretical basis for quadratic fit

$$D = \frac{4B^3}{\omega^2}$$

When the above factors are accounted for, the actual energy of a rovibrational state is

$$S(v,J) = \nu_0\left(v + \frac{1}{2}\right) + B_e J(J+1) - \alpha_e\left(v + \frac{1}{2}\right)J(J+1) - D_e[J(J+1)]^2$$



3040
3020
3000
2980
2960
2940
2920
Wavenumber (cm^{-1})
0
1
2
3
4
5
6
7
8
J
a0 = 2903.9 ± 0.35
a1 = 20.493 ± 0.204
a2 = -0.39286 ± 0.0246