Please read the theory and procedure for this lab in Shoemaker, Garland, and Steinfeld. However, the data workup can be much-simplified using polynomial curve fitting. Using the following hint to work up your data.

Equation 9 is a quadratic equation, that is, it is a second order polynomial. Least squares curve fitting works well for polynomials, just like it does for straight lines. A short cut is to use Equation 9 directly with 2nd order polynomial regression (least squares curve fitting). This will save some time compared to taking difference frequencies. It also provides better statistical uncertainties for the fit parameters. Therefore, all you need do is to input your indexed frequencies and do the polynomial fit.

The polynomial coefficients are related to the parameters in equation 9 as follows:

\[
\tilde{\nu} = \bar{\nu}_0 + (2B_e - 2\alpha_e) m - \alpha_e m^2 \quad \text{(9)}
\]

\[
y = c + bx + ax^2
\]

where

\[
c = \bar{\nu}_0 \quad b = (2B_e - 2\alpha_e) \quad a = -\alpha_e
\]

See below for an example polynomial regression using Excel and the “quadest.xls” spreadsheet. This spreadsheet is on the Chemserver and the course Web page. It is necessary, since most curve fitting programs don’t provide an estimate of the fit parameter uncertainties.
To do your curve fitting, paste your peak frequencies into the “quadest.xls” spreadsheet. Nonlinear curve fitting algorithms require an initial guess for the fit parameters. These guesses can often be quite bad and still result in a good solution. The spreadsheet starts with the guesses a=0, b=1, and c=0. If you don’t get reasonable fit values, you might need to try guesses that are close to the expected values. Given below are the “quadest.xls” curve fitting results. The guesses are in the first row. The final fit results are in the row labeled “new”.

\[ f(x) = a x^2 + b x + c \]

<table>
<thead>
<tr>
<th>guess coefficient</th>
<th>0</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>new coefficient</td>
<td>-0.305971537</td>
<td>20.39985273</td>
<td>2885.823255</td>
</tr>
<tr>
<td>uncertainty &quot;+-&quot;</td>
<td>0.002983592</td>
<td>0.018157459</td>
<td>0.195385111</td>
</tr>
</tbody>
</table>

The row labeled “uncertainty” lists the standard deviation of the fit results. Propagate the uncertainties through to your final results in terms of force constants and bond lengths. Rather than doing a careful propagation of errors treatment, however, you can just use significant figure rules. For example, from the printout above, we see that the fundamental vibration frequency is 2885.82±0.20 cm\(^{-1}\). Therefore, we know the fundamental vibration frequency to five significant figures.
The Generation of DCl

The method for generating DCl in Shoemaker, Garland, and Steinfeld is messy and generates a lot of chemical waste. A much simpler method is to use the reaction:

\[ \text{NaCl (s)} + \text{D}_2\text{SO}_4 (l) \rightarrow \text{DCl (g)} + \text{NaDSO}_4 (s) \]

using concentrated D$_2$SO$_4$, which is commercially available. Concentrated D$_2$SO$_4$, like concentrated sulfuric acid, is very corrosive. So be extremely careful to avoid spills. If any gets spilled, clean up the spill immediately with lots of water. A convenient apparatus for the reaction is shown below:

Procedure:
Add about 2 g of NaCl to a 25-mL round bottom flask. Use a gas cell with septa on the inlet tubes and CaF$_2$ cell windows. Some water and D$_2$O is generated that would fog normal NaCl cell windows, so we use CaF$_2$ windows instead. Connect the gas cell as shown. Fill a plastic syringe with about 2mL of concentrated D$_2$SO$_4$. When you fill the syringe, work quickly to avoid exposure to moisture in the air, which will exchange H$^+$ for D$^+$ ions and decrease the purity of your D$_2$SO$_4$. Reseal the D$_2$SO$_4$ bottle quickly and store in a dessicator. Insert the syringe needle through the septum on the 25-mL flask. Add the D$_2$SO$_4$ slowly, drop-by-drop at a rate that keeps the froth that forms from leaving the round bottom flask. Allow the gas cell to fill until the rate of frothing decreases. Then remove the needles from the gas cell. Make sure to wash the apparatus well, including the septa and tubing. Draw air through the syringe needles to make sure they are dry before storing.

Cleaning the gas cell: After you are finished with the gas cell, simply remove the septa in a fume hood and leave overnight to flush out. You don't need to wash the gas cell.