# SPECTRUM OF HCl AND DCl

Part of this experiment is described in S&G (5th ed. Expt.38, 6th, 7th and 8th eds. Expt.37).  However S&G discuss only the fundamental transitions ($\upsilon = 0 \to 1$) while with the instruments available here, data will be obtained also for the first overtone transitions ($\upsilon = 0 \to 2$).  This extra information allows for the unambiguous determination of some of the spectroscopic parameters.

## 1.  Safety

The benzoyl chloride vapours are very irritating to the eyes and throat; this compound must be handled inside the fume hood.

When handling liquid nitrogen, wear thick protecting gloves.  Read and follow carefully the instructions given to clean the apparatus at the end of the experiment.

Be aware that the glass trap containing the distilled mixture of HCl/DCl must be kept at liquid nitrogen temperature to prevent the pure acids to vaporize; this trap may burst if the content is allowed to warm up when all the valves are shut.

Wear eye protection at all times in the laboratory.  Wearing a lab coat is strongly recommended for this experiment.

## 2.  Preparation of HCl/DCl mixture

2.1  PREPARATION

To prepare DCl, proceed as described in S&G with the following modifications:

a)  scale the preparation by 1/2 to 1/3 (use a weighing bottle with its lid on to measure benzoyl chloride).

b)  spike with $\approx 0.5$ ml $H_2O$ the volume of $D_2O$ you are using in order to obtain a mixture of HCl/DCl as your product.

In this manner, spectra of both isotopic species can be collected with the same gas sample (the spectra are well separated and do not interfere with each other).  Do *not* use a heating mantle to heat up the flask containing the reaction mixture; instead use a hot air gun which allows a better control of the rate of heating.  The first trap contained a slurry of dry ice/acetone (temperature$\approx$ -80 C) which is cold enough to freeze and trap water but not the desired HCl (DCl) gas.  The second trap (liquid nitrogen, -195 C) when inserted, will freeze HCl (DCl) gas.  Test for HCl/DCl evolution by

holding a little beaker containing ~1 ml of concentrated ammonium hydroxide near the exit of the mercury bubbler and looking for white fumes of $NH_4Cl$; do not insert the liquid nitrogen trap around the collection flask until the white fumes have been observed.

## 2.2 FILLING THE GAS CELLS

*Before doing anything on the vacuum line, make sure that the cold trap which prevents corrosive gases from reaching the rotary oil pump, is indeed filled with liquid nitrogen.*

After completion of the reaction, attach the trap containing solid HCl/DCl to the vacuum line*. First remove any liquid air which may have condensed in the trap by pumping over the frozen gas while keeping the trap immersed in liquid nitrogen until a good vacuum is obtained. HCl/DCl will start to evaporate only when it is warmed up which is done by lifting the trap out of the liquid $N_2$. When sufficient HCl/DCl has been admitted to the cell, shut the trap outlet valve and replace quickly the trap into liquid $N_2$ (Why?).

## 2.3 CLEAN UP

At the end of the experiment, all surplus HCl/DCl should be allowed to evaporate in the fumehood. Do not allow these gases to reach the vacuum pump as they are very corrosive.

*When all your data have been collected and before you leave the lab, the cold trap has to be emptied. This involves:*

- *removing the liquid nitrogen dewar,*
- *switching the rotary pump off,*
- *venting the vacuum line (open the venting valve below the guard bulb),*
- *detaching the trap from the vacuum line (you may want to warm up the glass joint with a heat gun to soften the grease),*
- *finally placing the trap under the fume hood to let the frozen gases evaporate.*

Wash all the glassware before you leave. Ethanol is a good solvent for the end product, benzoic anhydride. Discard the wastes into the organic waste container; careful, the vapours of the anhydride are very irritating.

## 3. Data Collection

## 3.1 FUNDAMENTAL TRANSITIONS ($\upsilon = 0 \rightarrow 1$)

Attach the IR gas cell equipped with KBr windows to the vacuum line dedicated for gas handling (see Chem 366 lab manual, "IR of $SO_2$"

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* The vacuum line is the same one used for the IR spectrum of $SO_2$ in Chem 366.

experiment for details on this apparatus). Fill the cell with HCl/DCl to a pressure of ~100 torr and collect a spectrum on the BOMEM-FTIR (or the MATTSON FT-IR) instrument at the highest resolution available; set the number of scans to 64. Collect under the same conditions a spectrum of the evacuated cell to be used as reference. The HCl rotational spectrum is to be found between $2600 \text{ cm}^{-1}$ and $3100 \text{ cm}^{-1}$ while that of DCl between $1950 \text{ cm}^{-1}$ and $2200 \text{ cm}^{-1}$. The weak first overtone of the DCl spectrum is around $4000 \text{ cm}^{-1}$; for HCl, the first overtone is outside the range of the IR instrument. Obtain for each species a plot of the relevant spectra along with a listing of the position of the absorption lines.

3.2 FIRST OVERTONE TRANSITIONS ($\upsilon = 0 \rightarrow 2$)

*For DCl, data corresponding to the first overtone transitions may be obtained in the previous measurement using the FTIR spectrophotometer.*

Fill with HCl/DCl a 10 cm suprasil cell to ~1 atm. For HCl record the spectrum from 1850 to 1700 nm on the CARY 17-OLIS spectrometer. The instructor will brief you on how to use this instrument. Use a 1500 intervals and 40 reads/point. Fix the spectral bandwidth at 0.1 nm. Make sure that slit height knob is in "IR" position (pulled out). Record under the same conditions the DCl spectrum from 2500 to 2350 nm.

The instruments used in this experiment are delicate and easily damaged. The student must only use them under supervision by an instructor or the appropriate technician. Fill in the log books once all your data are collected.

## 4. Calculations

A large amount of data (eight spectral series in all) has to be organized since for each of the four isotopic species, $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$, both the fundamental and the first overtone spectra are available.

First, for each isotopic species tabulate and assign the vibrational and rotational quantum numbers corresponding to each of the observed absorption frequencies (expressed in $\text{cm}^{-1}$).

Second, process the data using *either* Method 1 or Method 2 *(not both)*.

4.1 METHOD 1

The data may be processed following S&G. However, the S&G treatment should be slightly modified to take into account the extra information coming from the overtone spectrum. Instead of using the equilibrium rotational constant $B_e$, one may use $B_\upsilon$, the rotational constant associated with each vibrational state $\upsilon$. The *term values T* (Eqn. 4 in S&G) are now written as:

$$T(\upsilon, J) = \tilde{\nu}_e(\upsilon + \tfrac{1}{2}) - \tilde{\nu}_e x_e(\upsilon + \tfrac{1}{2})^2 + B_\upsilon J(J+1) - D_e J^2(J+1)^2 \tag{1}$$

Following S&G, derive Eqn. 2 — the equivalent of Eqn. 9 in S&G — for the fundamental transitions*,

$$\tilde{\nu}_{0\to1}(m) = \tilde{\nu}_0 + (B_0 + B_1)m + (B_1 - B_0)m^2 - 4D_e m^3 \tag{2}$$

Where

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \tag{3}$$

then Eqn. 4 for the first overtone

$$\tilde{\nu}_{0\to2}(m) = \tilde{\nu}_0' + (B_0 + B_2)m + (B_2 - B_0)m^2 - 4D_e m^3 \tag{4}$$

where

$$\tilde{\nu}_0' = 2(\tilde{\nu}_e - 3\tilde{\nu}_e x_e) \tag{5}$$

As in S&G, the notation is $m = J + 1$ for the R branch, $m = -J$ for the P branch. Note that in Eqn. 2 and 4, $D_e$ the centrifugal stretching term has *not* been neglected (older edition of S&G do neglect this term).

According to Eqns (2) and (4), the functional dependence of $\tilde{\nu}$ on quantum number $m$ is a cubic. To obtain the spectroscopic parameters $\tilde{\nu}_e$, $\tilde{\nu}_e x_e$, $B_0$, $B_1$, $B_2$ and $D_e$ for all the various isotopomers (isotopically distinct species) one can fit each set of experimental data to a cubic (third order polynomial)[†] and match the polynomial coefficients given by the fit to the coefficients of the power of $m$ in eqns. (2) and (4). Depending on the quality of the data, one may have to limit the fit to a quadratic (second order polynomial) – effectively neglecting the centrifugal term $-4D_e$, which makes a small contribution.

### 4.2  METHOD 2

Alternatively, the data can be analysed using the EXCEL template HCLDCL.XLS available from some of the PCHEM computers or from the course web site.

First show that the transition energy, which is the difference between the two appropriate term values, is given by eqn. 6

$$\Delta E(\upsilon, J, \delta) = \tilde{\nu}_{calc}(\upsilon, J, \delta) = T(\upsilon, J + \delta) - T(0, J) =$$

$$\tilde{\nu}_e \upsilon - \tilde{\nu}_e x_e \upsilon(\upsilon + 1) + B_e[\delta(2J+1)] + \alpha_e[\tfrac{1}{2}J(J+1) - (J+\delta)(J+\delta+1)(\upsilon+\tfrac{1}{2})] +$$

$$+ D_e[J^2(J+1)^2 - (J+\delta)^2(J+\delta+1)^2] \tag{6}$$

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*Some references use the symbol $\omega$ instead of $\tilde{\nu}$ to designate frequency expressed as wavenumber.

[†]You may want to use the EXCEL template WPOLYFIT.XLS

where the vibrational quantum number $\upsilon$ is 1 for the fundamental transitions and 2 for the first overtone, $J$ is the rotational quantum number and $\delta = +/- 1$ for the R/P branch respectively)

The spreadsheet is designed to perform a simultaneous fit of both sets of data (fundamental and overtone) to Eqns. 6 for a given HCl species. One set of calculation uses a multi-linear regression and does not includes the centrifugal distortion term $D_e$. Actually, since this term is a non-linear function of other fitting parameters (Eqn. 8), a non-linear least squares method is also provided to obtain $D_e$ ; for this fitting technique to work, a "good" set of starting values for the fitting parameters needs to be provided.

## 5. Discussion

Determine whether the $B$ values can be represented by the linear formula (implicitly assumed in S&G's derivation)

$$B_\upsilon = B_e - \alpha_e (\upsilon + \tfrac{1}{2}) \tag{7}$$

If so, determine values of $B_e$ and $\alpha_e$. Determine whether there is any evidence for centrifugal distortion; if so, try to estimate $D_e$. Theory predicts (Ref. 1) that

$$D_e = \frac{4B_e^3}{\tilde{\nu}_e^2} \tag{8}$$

Do your results agree with this?

Using your experimentally determined spectroscopic parameters, calculate the predicted values for all the transitions you observed and generate a table of residuals $(\tilde{\nu}_{exp} - \tilde{\nu}_{calc})$. Plot these residuals versus $m$ (as $m$ is defined above and in S&G). Do you observe any trends in these plots? What can be said about the model used to analyse these spectra?

Answer the questions in S&G. In addition, determine the inter-nuclear distance in HCl and DCl. Calculate theoretical values for the H-D and $^{35}$Cl-$^{37}$Cl isotope splitting and compare with your experimental results. Present a table comparing your results with literature data.

Submit your raw data (peak position in nm or cm$^{-1}$) in electronic form (diskette or email) when handing in your report.

## 6. References

G. Herzberg, *Molecular Spectra and Molecular structure*, 2nd ed., Van Nostrand, N.Y.(1950).

P.R. Bevington and D.K. Robinson, *Data Reduction and Error Analysis for the Physical Sciences.*, 2nd ed. McGraw–Hill, N.Y., (1992).

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