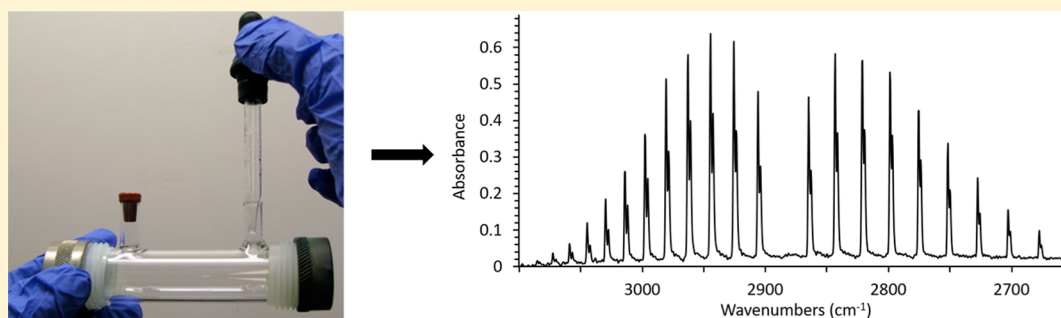


Simple Acid Vapor Method for Production of HCl and DCl Gas for IR Spectroscopy

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Supporting Information



ABSTRACT: We report here a method that utilizes the vapor pressure of HCl(g) above a concentrated HCl(aq) solution as an extremely simple and safe method to produce small amounts of HCl vapor in an IR gas cell. This vapor pressure approach can also be used to produce DCl(g) by introducing a few drops of concentrated DCl(aq) into the gas cell.

KEYWORDS: Upper-Division Undergraduate, Hands-On Learning/Manipulatives, IR Spectroscopy, Physical Chemistry, Laboratory Instruction

INTRODUCTION

In this *Journal* there has been interest over many years in the classic physical chemistry experiment that analyzes the infrared absorption, rotationally resolved vibrational spectrum of HCl in the vapor phase or sometimes a HCl/DCl vapor phase mixture. For the HCl molecule or a mixture of HCl and DCl molecules, an analysis yields the determination of molecular properties such as the bond force constant k , the moment of inertia I , and the bond length r_e .^{1,2} With sufficient resolution the unique ³⁵Cl and ³⁷Cl chlorine isotope properties can also be distinguished.^{1,2} The decades-long utilization of this experiment in the physical chemistry laboratory has resulted in many theoretical and computational analysis modifications and suggestions for this undergraduate laboratory experience.^{3–14} A summary of spectroscopic constants and uncertainties for H³⁵Cl, H³⁷Cl, D³⁵Cl, and D³⁷Cl from student infrared spectra has been given and shows the excellent results possible for this experiment and its associated data analysis.^{7,14}

The use of this experiment over more than 50 years has resulted in quite a variety of proposed experimental procedures to generate HCl gas or HCl and DCl gases and to do so by what often have been reported to be safer and/or simpler methods.^{15–28} We wish to review the various methods that have been used and then focus on the specific parameters associated with what we consider to be a simpler and safer method to load an IR gas cell with these diatomic molecules. We refer to adding a few drops of concentrated hydrochloric acid to the cell and then utilizing the vapor pressure of HCl(g) above a concentrated HCl(aq) solution to fill the cell.

In our opinion, this method represents the simplest and safest possible method to produce small amounts of HCl gas in an IR gas cell. Although this method has been mentioned by Pattacini,²³ it has been overlooked as a viable approach. Subsequent papers (discussed in detail below) have not used this method even as they referred to other experimental techniques that they sought to simplify. For this reason, we want to bring attention to the viability of this “vapor pressure method” to produce HCl gas to fill a gas IR cell. Our students have had at least 10 years of success with this approach, and it works well in an undergraduate laboratory setting. Because only the brief mention by Pattacini is available, the range of suitable experimental parameters (acid concentration, waiting time, number of drops) has not been reported. We wish to report these details to make this method more widely known for the physical chemistry laboratory. We also share that this method works as well with concentrated deuteriochloric acid to produce DCl(g). This vapor pressure method that we advocate avoids the use of any complicated apparatus and avoids any chemical reaction.

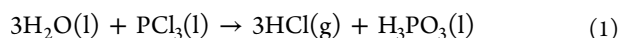
For many years in our Physical Chemistry I Lab, we included the infrared determination and analysis of H³⁵Cl and H³⁷Cl described in detail elsewhere^{1,2} after first generating and trapping HCl(g) in a 10 cm gas cell by the reaction of water

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and phosphorus trichloride to produce hydrogen chloride gas and phosphorous acid as shown below.



This reaction required setting up a glass manifold system with an aspirator vacuum and carefully monitoring the rate of production of HCl gas as water was added to the reaction. However, one time, out of curiosity, a few drops of concentrated hydrochloric acid were placed directly into the gas cell. After waiting a few minutes, a suitable spectrum with H^{35}Cl and H^{37}Cl splitting was observed. We then switched to this "acid vapor method" to fill an IR cell whenever this experiment was done. It was some years later before we realized that although this method had been briefly mentioned,²³ its utility as a simple and safe method to generate HCl(g) or DCl(g) had not yet been fully recognized or appreciated.

Over the past 50+ years a variety of methods to generate HCl(g) and/or DCl(g) have been reported.^{1,2,15–28} One direct method that has been used for some time is to employ an HCl gas cylinder with a gas-handling vacuum manifold system to fill a cell with HCl(g)^{1,2,16} or with solvation of HCl(g) in $\text{D}_2\text{O}(\text{l})$ to produce DCl(g).¹⁷ In addition to the need for a glass manifold system to charge a gas IR cell, there are obvious safety concerns for the routine undergraduate use of a high pressure HCl cylinder. The common method suggested for DCl gas production was to synthesize it from a reaction of benzoyl chloride $\text{C}_6\text{H}_5\text{COCl}$ and heavy water $\text{D}_2\text{O}(\text{l})$. This synthesis requires a glass manifold system and a vacuum system with a liquid nitrogen trap and careful monitoring of reaction pressure.²

It was reported that, instead of the reflux of D_2O and benzoyl chloride in a vacuum system, the preparation time was shortened by using the reaction of concentrated $\text{D}_2\text{SO}_4(\text{l})$ and 2 $\text{KCl}(\text{s})$ to form DCl(g) and $\text{K}_2\text{SO}_4(\text{s})$.²⁸ Two to three milliliter samples of $\text{D}_2\text{SO}_4(\text{l})$ were sealed in glass ampules for use during the semester to avoid D and H exchange from moisture in the air. The concentrated deuterio sulfuric acid was added dropwise to a three-necked flask with connections to aspirator vacuum line, manometer and cell, and a dropping funnel. Alternatively, an $\text{H}_2\text{SO}_4(\text{l})$ and $\text{D}_2\text{SO}_4(\text{l})$ mixture was used to produce HCl(g) and DCl(g).²⁸ Also suggested was to use a mixture of D_2O (99%) and concentrated HCl acid (36%) mixed for exchange of D and H isotopes along with a vacuum line with a manometer, reaction apparatus using two freeze–thaw cycles, and a 50 to 60 °C water bath to increase the vapor pressure with a collection to 20 to 30 Torr of a HCl(g) and DCl(g) mixture.²²

Procedures to produce HBr and DBr individually or with HCl and DCl have been proposed.^{19–21} One of these methods has been critiqued for using toxic and dangerous substances such as toluene- d_8 and liquid bromine,²⁰ while it has been argued that these problems make students more conscientious about safety.²¹

An early report suggested simply mixing a few drops of concentrated sulfuric and hydrochloric acids in a 10 cm quartz sample cell and generating HCl gas.¹⁵ H_2SO_4 acid can cause protonation of Cl^- to release HCl(g). That simple approach has been used in subsequent applications and has been shown to require concentrated hydrochloric acid.¹⁸ The HCl experiment has been employed as a miniproject using inquiry-based learning to enhance problem solving and learning skills. Zhobenko observed that due to isotopic

exchange rates that to achieve a 50:50 HCl to DCl gas ratio it was necessary to use a 10:90 ratio of H_2SO_4 and D_2SO_4 acids.²⁵

It has been reported that an improvement in the benzoyl chloride and water reaction was to heat benzoyl chloride with a 1:5 ratio of $\text{H}_2\text{O}:\text{D}_2\text{O}$ and then freeze the produced HCl/DCl gas in a liquid nitrogen trap.²⁶ This ratio was selected to adjust for the kinetic isotope effect and achieve roughly equal amounts of HCl/DCl. However, instead of freezing the sample in a liquid nitrogen trap, the gas was collected in a 3 L Florence flask to avoid the possibility of a sudden and dangerous positive pressure rise in the warming cycle.²⁶

A follow-up suggestion was made to further modify the safety risk and simplify by the use of microscale glassware.²⁷ This microscale method delivered a HCl/DCl gas mixture while also producing SO_2 gas by the reaction of thionyl chloride SOCl_2 with water or a water and deuterium oxide mixture. Mayer, Bard, and Cantrell used a nitrogen gas purge and then added water by a microliter syringe to thionyl chloride and allowed the product gas exiting the cell to bubble through an indicator solution to follow the progress of the reaction.²⁷ This change eliminated the need for a complicated gas and vacuum manifold system.

For the various methods used over the years, while simplifications have been suggested and safety improvements have been made, the elimination of any reaction and elimination of all apparatus and vacuum systems leads to what we believe to be the safest and simplest method to generate the desired gas. This acid vapor method also illustrates the sometimes overlooked equilibrium between the molecule gas phase and acid dissolved phases.

Detailed data for the partial pressures of hydrogen chloride and water over aqueous solutions of HCl based on temperature and concentration have been generated based on infrared spectroscopic measurements.²⁴ Elm, Zipprian, and Schaber's interests were in industrial design requirements and the limits of concentrations of volatile substances (HCl along with NH_3 and HBr) especially lower than 300 ppm. For example, at 41.2 °C, as the concentration of HCl in water by mass percent was changed from 15%, 9.0%, 6.1%, to 4.5% the associated partial pressure of HCl gas decreased from 0.149, 0.012, 0.0028, to 0.0011 Torr, respectively.²⁴ By comparison, the vapor pressures of water at the same conditions were reported to be 44.2, 51.3, 54.4, and 55.9 Torr.²⁴

More useful because of its higher acid concentrations is the early data set based on the calculations (not direct measurements) of Fritz and Fuget.²⁹ Using electrochemical data, Fritz and Fuget estimated the vapor pressure of HCl over a wide range of hydrochloric acid concentrations and 10° temperature increments from 0 to 50 °C. For example, at 20 °C, for concentrations of 12.0, 10.0, 8.0, 6.0, and 1.0 M, Fritz and Fuget calculated the HCl(g) pressures to be 11.8, 2.83, 0.56, 0.090, and 0.00015 mmHg, respectively.²⁹ Thus, it becomes clear why more concentrated acid solutions are needed to get suitable HCl(g) pressures. However, it also becomes clear that no special apparatus or reaction is required to generate HCl(g) for IR spectral analysis.

■ MATERIALS AND METHODS

The IR gas cell (Gas Cell –10 cm Pathlength, RJ Spectroscopy Co.) is assembled and a rubber septum is placed over one of the two side arms of the gas cell. The empty gas cell is placed on the long-arm cell holder in the Fourier Transform Infrared

Spectrometer (FT-IR) (Nicolet 380 FT-IR, Thermo Electron Corporation). A background spectrum on the empty cell is obtained (Resolution = 1 cm^{-1} , Number of Scans = 16). The cell is removed from the instrument to perform the next few steps in the hood.

Three to six drops of HCl or DCl with a 12 M concentration is added to the bottom of the gas cell. Hydrogen chloride gas turns wet litmus paper from blue to red, so litmus paper placed in one of the side arms of the gas cell provides a quick detection of HCl or DCl vapor. A septum is placed over the open side arm of the gas cell. This process is done while carefully keeping the cell level so as to not let the HCl or DCl touch the NaCl salt windows at either end of the gas cell. The apparatus to generate the HCl(g) or DCl(g) for IR spectroscopy is shown in Figure 1.

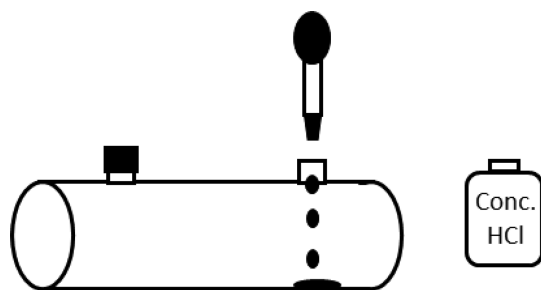


Figure 1. Vapor pressure method for capturing HCl vapor in the IR gas cell.

The vapor from the HCl or DCl quickly reaches an equilibrium within the gas cell before it is placed into an IR spectrometer. After reaching equilibrium in about 5 min, the FT-IR spectrometer is used to obtain a spectrum of the HCl or DCl in the vapor phase. IR spectra are recorded over 16 scans at 1 cm^{-1} resolution. If the desired spectrum in the 2600 to 3100 cm^{-1} region for HCl or the 1950 to 2200 cm^{-1} region for DCl is not obtained, then waiting to let more HCl or DCl go into vapor phase or adding more drops of liquid is required.

Each week the students doing this experiment assemble, use, disassemble, and then clean the cell. The student's laboratory handout regarding assembling and cleaning the cell is given in the Supporting Information.

HAZARDS

Both the HCl and DCl solutions and gases have a corrosive effect on human skin. Personal protective equipment such as goggles and gloves are required to minimize risks when handling in the hood. When finished, the gas cell is carefully disassembled in the hood and any remaining HCl solution is disposed of in a marked waste bottle.

RESULTS AND DISCUSSION

The IR absorption spectrum of the HCl(g) is shown in Figure 2. It also shows two sets of peaks due to H^{35}Cl and H^{37}Cl .

Similar experiments may be performed by replacing concentrated HCl(aq) with DCl(aq). The IR absorption spectrum of the DCl(g) from DCl(aq) is shown in the 1900 to 2200 cm^{-1} region in Figure 3a as well as the spectrum of the HCl(g) in the 2600 to 3100 cm^{-1} region due to hydrogen–deuterium exchange. The more intense set of peaks arise from DCl(g) as it is the more abundant. Different groups of students may obtain a less intense set of peaks from DCl(g) as DCl(aq)

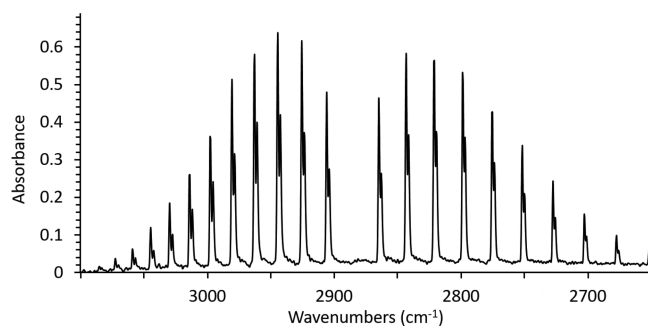


Figure 2. IR absorption spectrum of the fundamental band for HCl.

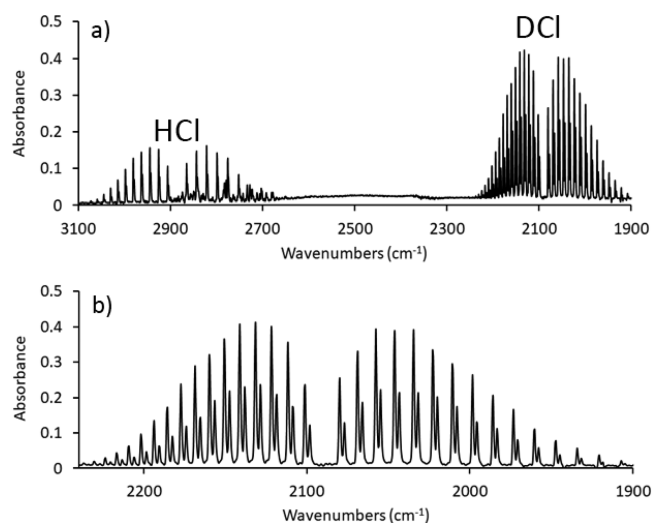


Figure 3. (a) Infrared absorption spectrum to show HCl and DCl peaks produced. (b) Fundamental absorption band of DCl.

is exposed to air longer. Figure 3b shows two sets of peaks due to D^{35}Cl and D^{37}Cl .

The laboratory reports written by students provide evidence that IR spectra of HCl are consistently obtained without difficulty. Instructional modifications have been performed to find the most intense absorbance peaks, which include the specific variables of waiting time, acid concentration, and the number of drops. Absorbance intensity reached the maximum with 5 drops and did not increase with extra drops. A convenient waiting time after adding HCl(aq) is 5 min to obtain good absorbance peaks. Reducing the concentration of HCl(aq) from 12 to 10.5 M to 9 to 7.5 M decreases the absorbance of the comparison peak (2944.5 cm^{-1}) from 0.569 to 0.190 to 0.095, respectively (see Table 1). No readable spectrum was observed at 6 M HCl(aq).

The HCl(g) absorbance peak (2944.5 cm^{-1}) values (see Table 2) only varied from the mean of these values by $\pm 12\%$ from 2 drops to 20 drops. Table 2 data are based on using 12

Table 1. HCl Concentration vs Absorbance with 5 Drops of HCl and 5 Min Waiting

HCl Concentration (M)	Absorbance at 2944.5 cm^{-1}
12	0.569
10.5	0.190
9	0.095
7.5	0.059
6	N/A

Table 2. Number of HCl Drops vs Absorbance with 12 M HCl and 5 Min Waiting

Number of HCl Drops	Absorbance at 2944.5 cm ⁻¹
2	0.460
3	0.547
5	0.638
10	0.591
20	0.546

M HCl and a 5 min wait for spectrum acquisition. The highest absorbance was observed for 5 drops but 3 drops gave about 85% as large absorbance. So, very little acid is required to obtain sufficient HCl(g) for analysis.

Whether the spectrum was acquired after a 3 min delay or up to a 20 min delay after adding 5 drops of 12 M HCl acid to the cell, the absorbance at (2944.5 cm⁻¹) only varied from the mean of the tested times by $\pm 1.7\%$. Thus, a cell with drops of acid added proved to be a very time stable technology for HCl(g) analysis.

If there is a special interest in the use of a pure gas or a special reaction or techniques that might involve utilizing a gas manifold, vacuum system, freeze–thaw cycles or other special methods, then it would be appropriate to use any of the varied techniques discussed in the **Introduction**. However, if the desire is to generate enough HCl(g) or DCl(g) to obtain and analyze gas phase data, then what we have illustrated is, we believe, the simplest and safest technique. We have used it for HCl and HCl/DCl mixture but have not tried it for HBr or DBr. Everything is eliminated except the gas cell. No special apparatus, no gas cylinders, no chemical reactions, no complicated procedures, and no vacuum systems are required. This method may be accessible for other gases, such as HBr, DBr, or NH₃, in equilibrium with an aqueous phase, and may be of interest for further consideration.

CONCLUSION

We report here a method whereby the vapor pressures of HCl(g) above a few drops of concentrated hydrochloric acid 12 M HCl(aq) and DCl(g) above a few drops of concentrated deuteriochloric acid 12 M DCl(aq) are sufficient to fill a 10 cm path length IR gas cell. This *acid vapor method* eliminates the complications (gas manifold, pump, special glassware, special reactions, etc.) associated with many of the previously reported methods. The amount of vapor present in the IR cell works well for determining the infrared absorption, rotational–vibrational spectrum of these heteronuclear diatomic molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.8b00431.

Laboratory handout in physical chemistry (PDF)

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Notes

The authors declare no competing financial interest.

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