Paper

The classic HCl experiment: how long is the hydrogen–chlorine bond?

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The analysis of the rotational-vibrational spectra of hydrogen chloride has been utilised over many years to provide valuable learning experience for chemistry students. This paper describes a physical chemistry laboratory mini-project based on the classic HCl experiment as an example of enquiry-based learning aiming to achieve a better understanding of molecular spectroscopy by the students and to enhance their problem solving and independent learning skills. The experiment itself has been extended to the preparation of HCl and DCl, handling of the gaseous samples and analysis of both the fundamental and the first overtone bands in the infrared spectra. Working in small groups, students develop their own research strategy, carry out the experiment, analyse the data and make conclusions about the effect of isotopic substitution on the bond length and the bond force constant of hydrogen chloride. A number of mini-projects have now been introduced to our spectroscopy and physical chemistry courses. In addition to improving students' knowledge of the subject, problem solving and team working skills, they also bridge the gap between scripted practicals in the first year teaching laboratory and the research projects conducted by our students in their final year at Keele.

Introduction

Over the last forty years, the analysis of the rotational-vibrational spectra of hydrogen chloride has become a classic experiment in physical chemistry laboratories.[1, 2, 3, 4, 5] Indeed, a number of molecular and vibrational parameters can be obtained from such measurements with a high degree of precision, and a clear link between the quantum chemistry theory and spectroscopic experiments can be established. Some more recent developments of this experiment include the use of more sophisticated analysis routines, the investigation of deuterium chloride and computer modelling of the rotational-vibrational spectra of diatomic molecules.[6, 7, 8, 9] At Keele, we have recently introduced a number of physical chemistry laboratory mini-projects for our undergraduate students in order to enhance their skill base, problem solving and independent learning.[10] In general, a mini-project commences with setting a problem related to studied topics: to investigate the effect of isotopic substitution on the bond length and the bond force constant, to construct a quantitative Jablonski diagram for an aromatic molecule, etc. In the following step, students need to develop their own research strategy that outlines how they are going to conduct the experiment, obtain the required information and analyse the data. In the course of the practical work carried out in small groups, students need to reflect on the approach, make improvements to the experimental design and learn from their own mistakes. Finally, an individual or a group report for each experiment is submitted; in the latter case, a self-evaluation of the teamwork has to be included. It should be noted that despite all the modifications, the practical work still does not require the use of expensive chemicals, sophisticated equipment or highly specialised instrumentation. Following this approach, four experimental mini-projects on various topics in vibrational and electronic spectroscopy have now been incorporated into the laboratory classes for our second year chemistry students. This paper describes one of the projects, a modified HCl experiment, as an example of enquiry based learning, which is aiming to ensure a better understanding of molecular spectroscopy by the students and to stimulate their active involvement in the learning process.

Experimental Procedures and Background Theory

The HCl mini-project was undertaken over three 2-hour sessions including planning the work and carrying out the experiment and data analysis. In addition, about the same amount of private study time was necessary for background reading, information retrieval and writing the final report. Access to standard teaching laboratory facilities and information resources was also required. The classic HCl experiment has been substantially extended to include the preparation of both HCl and DCl, handling of the gaseous samples for spectroscopic measurements and analysis of both the fundamental and the first overtone bands in the infrared spectra. FTIR transmittance measurements were performed using a Thermo Nicolet Avatar 320 and a Perkin-Elmer Paragon 100 instruments, both of which are entry level FTIR spectrometers commonly available in the undergraduate chemistry laboratories. The details of the sample preparation, spectra collection and data processing are described in the available supplementary information.[11]

Laboratory Class: Day One

Instead of a traditional style detailed laboratory script describing the background theory, experimental procedures and data analysis over many pages, students receive a one-page summary of the task.

"Studying chemistry we are routinely considering detailed structural features of organic and inorganic compounds. Have you ever wondered where all this information came from? Who determined bond lengths, geometry and composition for thousands and thousands of molecules, when and how? Well, here is your chance to follow the footsteps of many distinguished researchers.

Your aim in this experiment is to determine the hydrogen–chlorine bond length for four isotopic analogues $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$ to ±2 pm. In addition, you need to determine the hydrogen–chlorine bond force constant for these molecules. Based on your data, you need to draw conclusions about the effect of isotopic substitution on the bond length and on the bond force constant.

In this mini-project you are expected to demonstrate practical skills in experimental chemistry and data analysis as well as the ability to plan your work and to manage your time and team effort.

You should work in groups of 3 or 4. First of all, you need to develop a plan outlining your research strategy: how you are going to conduct the experiment, analyse the data and obtain the required information. Keep in mind the resources available in the laboratory when planning your work. Before commencing the experimental work, you must discuss your plan with a demonstrator who may provide additional instruction sets and assigned exercises.

Following the discussion, you will need to complete a risk assessment, carry out the experimental work, analyse your data and calculate the required values for bond lengths and bond force constants in order to achieve the aim of the experiment, and produce a report."

When the initial perplexing reaction subsides and the students proudly reject the offer of a one-meter wooden ruler for the bond length measurements the teamwork begins. By the end of the first lab period, detailed plans of actions are drawn up and discussed, and the preparations for the experimental work are underway.

Making It with Spectroscopy

Before long students realise that their molecular spectroscopy course provides a solid theoretical foundation for the analysis of molecular structures and that the FTIR spectrometers available in the teaching laboratory can provide good quality rotational-vibrational spectra of simple molecules in the gas phase. They also discover that the sample of hydrogen chloride is not supplied but must be prepared first, which requires some revision of first year chemistry. Since they are required to obtain four isotopic varieties of hydrogen chloride, students need to appreciate that ^{35}Cl and ^{37}Cl isotopes are naturally found in the 3:1 ratio (75.8% and 24.2%, respectively), whereas the abundance of deuterium is far below 1% (99.98% of ^{1}H and 0.02% of D) and the use of deuterated reagents is necessary.[12] It is also pointed out by the demonstrator that in order to produce an approximately 50:50 ratio of HCl to DCl in the isotopic mixture, one has to work with a 10:90 mixture of H_2SO_4 and D_2SO_4. This should lead to the discussion of the zero point energy and the effect of isotopic substitution on the dissociation energy and the reaction rates; if it does not, the instructor initiates it.

To reach the final destination and to obtain the required bond lengths and bond force constants students need to have a good grasp of the background theory, which provides a direct link to the lecture material and tutorials. Subsequent step-by-step analysis of the experimental data offers an opportunity to consider the experimental design and the underlying principles of molecular spectroscopy. For instance, the provided 'detailed' instruction tells students to collect infrared spectra using the highest available resolution. Which one is it, 1 cm^{-1} or 32 cm^{-1}? To keep students on the right track during their practical work and data handling, four sets of instructions are available, but not before students' working plans are finalised. A typical set of instructions describes a selected topic, e.g. sample preparation or data acquisition and processing, as it would in a comprehensive lab script, but with some key points missing or with additional compulsory questions initiating further discussion and testing the level of understanding of the background theory. In some cases students can gain 'bonus marks' (up to 10-15%) for being able to work out the difficult bits by themselves. Our instructions for the HCl mini-project cover the preparation of an isotopic mixture of $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$ and $D^{37}Cl$, the measurement of the rotational constants B_1 and B_o by the method of combination differences, the calculation of the rotational constant B_e, and the determination of the equilibrium vibrational frequency.[11]

The data treatment, although based on a rather simple model, is quite extensive, as results for all the isotopic variants of HCl have to be analysed. There is room here for the students to demonstrate their organisational skills and teamwork (each group of students can submit a joint account of their work which would have to include a self-assessment of the group's performance). IT competence and a reasonable background in math are also among important assets for this mini-project. Table 1 gives a summary of the subject specific and generic skills students are expected to demonstrate and enhance in this mini-project.

Table 1. Theoretical issues, experimental work and generic skills addressed in the HCl mini-project.

Subject specific knowledge	**Practical work**	**Generic skills**
Molecular spectroscopy of diatomic molecules Rotational and vibrational energy levels, population of energy levels Rotational and vibrational absorption spectra Isotopic substitution, bond length and bond force constant Fundamental transitions and overtones Harmonic and unharmonic oscillator Method of combination differences Preparation and properties of hydrogen chloride Isotopes, their properties and abundance Kinetic isotope effect	Sample preparation using isotopically substituted compounds Risk assessment Practical work with FTIR instrumentation Handling of gaseous samples for infrared analysis Work with specialised spectroscopic software	Working efficiently as a team Planning and managing own work and time Designing and planning an experiment Critical evaluation of own work Information retrieval from on-line resources and research papers Plotting graphs and obtaining statistical information

Finally, a conclusion should be reached whether isotopic substitution has any effect on the bond length and on the bond force constant. Accurate results for all four molecules, which usually agree with the literature data[5, 13, 14, 15] to ±1% (e.g. the bond length measurements are within 1 pm of the published values) greatly facilitate the decision making. Interestingly, students are often surprised to discover during discussions with the instructor that these data constitute some of the most accurate measurements they obtain in the undergraduate laboratory classes.

Concluding Remarks

Overall, students appreciate the challenge of this practical course that provides a clear link between the theory of quantum mechanics, spectroscopic analysis and everyday chemistry. They acknowledge difficulties encountered in their work and value the sense of achievement when the final conclusions are made, as well as the opportunity to develop critical thinking and ability to tackle unfamiliar and open-ended problems, which is clearly seen from their comments. To quote some of the responses, "*problem solving and team work provide an effective way of understanding course material and learning useful transferable skills*", "*new style makes lab more interesting*", "*labs enable you to use your own initiative and to apply your knowledge*", "*this is good experience for later in the course, i.e. research*", "*good practice in using team work – a vital skill*". In the module evaluation questionnaires, students emphasise that the mini-projects have helped them to enhance their skill base, to understand the background theory, to put the lecture material into context and to improve their team working. In addition, we are now accumulating more quantitative information, including the results for Spectroscopic Methods and related modules, marks for the exam questions on molecular spectroscopy, and of the students' performance in the final year projects, to assure successful learning outcomes of this approach.

Notwithstanding our generally positive experience with mini-projects, the following points should be kept in mind. Detailed planning and adequate resourcing of chemical laboratory mini-projects call for careful consideration. Some weaker students are likely to require additional attention and help to overcome the 'activation barrier'. It is worth noting that the current Internet culture encourages students to commence their enquiry based learning by hitting the Google search button, and they may be 'lucky' to find detailed answers on the web pages of some universities. To overcome this problem, the emphasis is placed on the students' explanation and understanding rather than on their ability to find the information. It has also become clear that students greatly appreciate the importance of teamwork, and they are now requesting additional training in team building and management techniques. This will be provided jointly with our Education Department as part of the key skills training for the second year students starting with the next academic session. In addition, a number of students have pointed out the demanding nature of the mini-projects ("*more time should be given to research the project*", "*thrown in the deep end*", "*it would help for a bit more background information, clues [to be given]*") and asked for more guidance and explanations at the beginning of the laboratory work to ensure smooth running-in for the molecular spectroscopy practicals.

Mini-projects are now becoming a common feature of our spectroscopy, inorganic chemistry and physical chemistry courses with around ten different experiments available in this format. These include four topics on molecular spectroscopy (*How long is the hydrogen-chlorine bond*, *The structure of acetylene, Conquering the spectrum of iodine*, and *The Jablonski diagram of anthracene*), two mini-projects on the chemistry of transition metal complexes and another four on electrochemistry and kinetics. In addition to boosting students' understanding of the subject, their generic and teamwork skills, the mini-projects serve as an important transition from scripted practicals in the first year to the research projects carried out by the chemistry finalists in their third year at Keele.

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