Determining the Speed of Sound and Related Heat Capacity Ratios of Gases Using Acoustic Interferometry and Molecular Electronic Structure Calculations

A Physical Chemistry Cloud Laboratory

Jeffery L. Yarger, School of Molecular Sciences, Arizona State University, Tempe, AZ 85287-1604.

OBJECTIVE: Physical chemistry typically starts with an introduction to gas properties, with an emphasis on molecular concepts and thermochemistry. This physical chemistry laboratory aims to complement lecture material through a combined (i) computational, (ii) experimental and (iii) data science (data and error analysis). In this lab, students are asked to use computational (electronic structure calculations) and remote experimental (acoustic interferometry) techniques to acquire data that allows for a determination of the speed of sounds and related thermodynamic properties (i.e., adiabatic index and heat capacity ratio) for one or more common atmospheric gases (e.g., He, N_2, CO_2 and Ar). Also, a common refrigerant gas will be provided as part of the remote acoustic interferometer setup and students should be able to use their experience with measurements on known gases to accurately determine the sound velocity, adiabatic index, and heat capacity ratio. This lab is designed to teach general laboratory problem solving and data/error analysis skills. *The goal of this lab is not only to practically learn how to acquire and analyze physical chemistry data, but also importantly, to understand how the molecular composition of a gas determines the speed of sound waves passing through it.*

INTRODUCTION

Of the three states of common molecular aggregation, only the gaseous state allows a comparatively simple quantitative description. Hence, the reason it is often emphasized in physical chemistry.[1,2,3] The aim of physical chemistry is to quantitatively interpret the observed properties of macroscopic systems in terms of the kinds and arrangements of atoms or molecules that make up these systems. Structurally, gases are nature's simplest substances; a simple model and elementary calculation yields results in good agreement with experiment. The kinetic theory of gases provides a beautiful and important illustration of the relation of theory to experiment, as well as of the techniques that are commonly used in relating structure to properties.[4]

In this lab, students will explore the molecular and thermodynamic properties of gases (molecular models of common gases shown in figure 1) by measuring the speed of sound and using the experimental measurements to calculate the ratio of the heat capacity of a gas at constant pressure to that at constant volume (C_P/C_V).[5] Often several gases are studied, and the results are analyzed and interpreted in terms of molecular theory (e.g., molecular degrees of freedom). The background material on heat capacity of gases is covered extensively in physical chemistry textbooks[2] as well as numerous sources online including Wikipedia, which is an excellent resource for all background material associated with this lab.

The goal of CHM 343 is to reinforce physical chemistry concepts through experiment. This includes both laboratory and computational experiments. Independent research skills and exploration is always allowed and even encouraged in upper division science labs. For example, (i) students can do a DIY acoustic interferometer as an alternative to using the remote system, (ii) students can explore alternative computational methods and applications, (iii) and students can choose a different set of gases for computational and experimental measurements. We encourage students to explore alternative experimental and/or computational methods and will always give added weight to students that go beyond following the exact procedures that are suggested. Okay, lets breakdown the computational, experimental, and data/error analysis components for this lab.

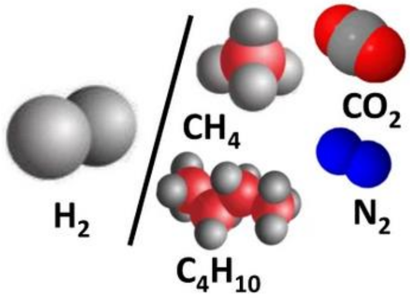

Figure 1 - Space filling model for several common molecular gases.

COMPUTATIONAL

Use quantum mechanics-based computational methods to calculate the thermochemical properties for several molecular gases. The goal is to do computational 'experiments' to estimate the heat capacity of several gases that will be experimentally measured using an acoustic interferometer (e.g., Ar, N_2, O_2, CO_2, and common refrigerant gases: CH_2F_2, CH_2FCF_3, $C_3H_2F_4$). Computational chemistry methods allow the contributions of translational, rotational, and vibrational degrees of freedom to be individually computed. An example of a simple online browser-based tool for basic molecular computation is MolCalc (https://molcalc.org).[6] A more in-depth discussion of computational software is provided at the biopchem.education website. ASU online students can also obtain an ASU supercomputer accounts on Sol and access to WebMO and computational packages such at Gaussian for any advanced computation chemistry experiments.

EXPERIMENTAL

- Using an acoustic interferometer, measure the white noise resonant sound spectra for one atomic gas (i.e., Ar), one common atmospheric molecular gas (i.e., N_2, O_2, or CO_2), and one common refrigerant gas (e.g., CH_2F_2, CH_2FCF_3, $C_3H_2F_4$).[5] A remotely accessible acoustic interferometer has been setup at ASU and will be made available to students. An accurate and precise length of the acoustic interferometer cavity is a critical parameter and will either be provided to students or needs to be determined using a gas with a well-known sound velocity. Argon or nitrogen gas both have very well-known sound velocities and can be used as the calibration gas to determine the acoustic interferometer tube length. With the accurate acoustic interferometer length determined or provided, all other acoustic interferometry measurements of various gases can be used to determine a precise speed of sound for gases at specific temperatures (the sound velocity is temperature dependent).
- Using acoustic interferometry with a calibrated length, determine the speed of sound propagation for an 'unknown' refrigerant gas that will be provided for the remotely accessible instrument. The measured sound velocity can then be used to calculate the heat-capacity ratio for any gas purged into the acoustic interferometry tube (data analysis). From the remote experimental measurements and data analysis, determine as many thermochemical properties as possible and make a hypothesis about the molecular identity of the unknown gas. If you are using a DIY acoustic interferometer, use Dust Off (Electronic Duster) as the unknown refrigerant gas.
- To make more of a connection between computational and experimental components, it is recommended that either FT-IR or Raman be collected on the refrigerant gas (and on CO_2, N_2O, Natural gas, or any other molecular gas).

DATA & ERROR ANALYSIS

- Make a figure with the molecular representations of the molecular gas(es) used for the computational experiments.[6,10] Further summarize the computational heat capacity and thermochemistry results in a table with a caption that provides a good summary of the computational details.[11–15]
- Make a figure with representative raw data obtained from the acoustic interferometry experiments and the sound spectrum (FFT processed data).[5,16–18] Use the sound spectrum to determine resonant frequencies (nodes). In general, error is reduced by measuring as many resonance node frequencies as possible. Plot the resonance node number versus the corresponding resonance frequency and use a least-squared fitting routine to show the best linear fit (show the fit and provide the linear best fit slope and intercept values and R^2). This now allows the calculation of the speed of sound (from the slope of the linear fit). Optimized fitting paraments and associated errors for all gases and one or more known and measured temperatures.
- Calculate the ratio C_P/C_V (γ, the adiabatic index) using the sound velocities determined in the step above. This should be done assuming an ideal gas equation of state (EoS). As an extra credit component, students can also use a real gas EoS such as the van der Waals (vdW) EoS.
- Translational, rotational, and vibrational contributions can be determined through the computational exercise as well as classical and quantum theory. Also, a predicted C_V can be determined from ideal gas and vdW gas EoS assumptions.
- Use standard propagation of error techniques to report error associated with all measurements and subsequent calculations and data fitting.[2,19–22] All reported numbers should have the associated +/- error and units.

LABORATORY REPORT/ NOTEBOOK

Students can write a standard laboratory report or use a modern electronic notebook (e.g., google colab), which can be used for all text descriptions, tables, plots, figures, data analysis, error analysis, discussion, and references. A detailed description and rubric for student lab reports is provided in the syllabus. It is important to not just report the results of experiments and computations, but also to discuss the insights obtained, keeping in mind the primary objective of this laboratory project:

The goal of this lab is to understand how the molecular composition of a gas determines the speed of sound waves passing through it. The speed of sound in an ideal gas only depends on its temperature, mass and adiabatic index (or heat capacity ratio). It makes intuitive sense from basic introductory chemistry concepts (e.g., kinetic theory of gases) that the sound velocity would be dependence on temperature and mass. But what does the adiabatic index (heat capacity ratio) have to do with it? The emphasis of this lab is for students to explore (computationally and experimentally) and hopefully 'discover' the connection and hence be able to explain the relationship between molecular structure/dynamics and its effect on heat capacity and sound waves passing through it. Finally, students should be able to put these molecular insights to bare for understanding the molecular thermodynamics of what makes a 'good' refrigerant gas.

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