6-1-2015

Research for the Advancement of Green Chemistry Practice: Studies in Atmospheric and Educational Chemistry

Steven Gene Cullipher
University of Massachusetts Boston

Recommended Citation

Cullipher, Steven Gene, "Research for the Advancement of Green Chemistry Practice: Studies in Atmospheric and Educational Chemistry" (2015). *Graduate Doctoral Dissertations.* Paper 203.

RESEARCH FOR THE ADVANCEMENT OF

GREEN CHEMISTRY PRACTICE:

STUDIES IN ATMOSPHERIC AND EDUCATIONAL CHEMISTRY

A Dissertation Presented

by

STEVEN GENE CULLIPHER

Submitted to the Office of Graduate Studies,
University of Massachusetts Boston,
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

June 2015

Green Chemistry Program

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Approved as to style and content by:

Hannah Sevian, Associate Professor
Chairperson of Committee

Timothy Dransfield, Lecturer
Member

Jonathan Rochford, Assistant Professor
Member

Nicholas Anastas, Ph.D., EPA
Member

Bela Török, Program Director
Green Chemistry Program

Robert Carter, Chairperson
Department of Chemistry

ABSTRACT

RESEARCH FOR THE ADVANCEMENT OF GREEN CHEMISTRY PRACTICE: STUDIES IN ATMOSPHERIC AND EDUCATIONAL CHEMISTRY

June 2015

Steven Gene Cullipher, B.A., Florida Gulf Coast University
M.S., Florida Gulf Coast University
Ph.D., University of Massachusetts Boston

Directed by Professor Hannah Sevian and Professor Timothy Dransfield

Green chemistry is a philosophy of chemistry that emphasizes a decreasing dependence on limited non-renewable resources and an increasing focus on preventing pollution byproducts of the chemical industry. In short, it is the discipline of chemistry practiced through the lens of environmental stewardship. In an effort to advance the practice of green chemistry, three studies will be described that have ramifications for the practice. The first study examines the atmospheric oxidation of a hydrofluorinated ether, a third-generation CFC replacement compound with primarily unknown atmospheric degradation products. Determination of these products has the potential to impact decisions on refrigerant usage in the future. The second study examines chemistry students’ development of understanding benefits-costs-risks analysis when presented with two real-world scenarios: refrigerant choice and fuel choice. By studying how benefits-costs-risks thinking develops, curricular materials and instructional approaches can be designed to better foster the development of an ability that is both necessary for green chemists and important in daily decision-making for non-chemists. The final study uses eye tracking technology to examine students’ abilities to interpret molecular properties from structural information in the context of global warming. Such abilities are fundamental if chemists are to appropriately assess risks and hazards of chemistry practice.

ACKNOWLEDGEMENTS

It was the best of times, it was the worst of times, it was the age of wisdom, it was the age of foolishness, it was the epoch of belief, it was the epoch of incredulity, it was the season of Light, it was the season of Darkness, it was the spring of hope, it was the winter of despair, we had everything before us, we had nothing before us…

- Charles Dickens, *A Tale of Two Cities*

I would be more than a little surprised if this is the first time Dickens' opening paragraph was quoted in a Ph.D. dissertation. It sums up my experience in graduate school very appropriately. This has been an extraordinary journey that has included both the best and worst moments of my life. I questioned my path at many times along the way as I imagine most doctoral students do. Yet here I stand at the finish line, proud of my accomplishments and forever grateful to the individuals who helped me to get here. It is a pleasure to have the opportunity to acknowledge these colleagues and friends.

I am most grateful to the best mentor that any graduate student could dream to have: Hannah Sevian. Not only is she a mentor, she is a scholar, an educator, an editor, a mother, a wife, and an inspiration. In spite of, or perhaps because of, the many roles she has to fill, she is a complete miracle worker. It has been a privilege and an honor to receive guidance from such a brilliant mind. I know that my career—and the education of all my future students—has been vastly improved because I have known her. She still has one secret she has yet to share with me, which will likely remain a mystery forever: how does she do it all?

Timothy Dransfield has inspired me more than he knows. During my first semester at UMass Boston, I was a wandering graduate student, undecided about the type of research I wanted focus on. I knew that green chemistry was my passion, but there were so many aspects of the philosophy that called to me. It was during one of his lectures on atmospheric chemistry that I decided I wanted to work with him. Tim displayed a level of passion in his teaching that I had not yet experienced as a graduate student – a passion that gave me a rudder and a course at a time when I needed it most. He has pushed the boundaries of my knowledge and experience to new levels, a skill that I hope to adopt for my own career.

The balance of my committee, Jonathan Rochford and Nicholas Anastas, have been patient and kind through the process of my studies. They stepped into the world of chemistry education research from their respective fields of inorganic chemistry and toxicology without hesitation. I appreciate their service on my committee and their mentorship along the way.

I would also like to express my gratitude to the faculty and staff of the Chemistry Department. Jason Evans was a valuable source of advice and information in his role as Graduate Program Director. My instructors, Nicholas Anastas, Robert Carter, Timothy Dransfield, Jason Evans, Michelle Foster, Jonathan Rochford, and Wei Zhang, gave me critical domain knowledge on which to found my career. The department staff, including Virginia Mackay, Dominique Altarejos, Liliana Teixeira, Paul Saniuk, Ryan Fitzgerald, and Rita Lam not only gave me essential administrative support, but also lent a kind ear on multiple occasions.

The members of the Sevian research group provided encouragement, solace, and friendship during especially challenging times of my graduate career and were eagerly willing to provide feedback on manuscripts, grants, presentations, and the occasional off-the-wall idea. In particular, Courtney Ngai–my work wife–has been a calm and tranquil rock, often providing me with some necessary grounding. My thanks also go to my oft-partner-in-crime Gabriela Szteinberg, who kept my spirits high and gave me much needed motivation.

I also wish to thank many collaborators, colleagues, and impromptu mentors for being a source of scholarly stimulation: Vicente Talanquer and Melissa Weinrich of the University of Arizona; Shainaz Landge and Janessa Dunn of Georgia Southern University; Heilen Arce and Paula Brenes at the University of Costa Rica; and Sarah Hansen of Columbia University.

Though I am not a Florida native, it was my home for many years. Packing up to move to New England to continue my education was a very difficult decision. I wish to thank the friends I have gained along the way who have made Boston feel like my true home, particularly Stephen Brodeur, my fellow graduate students, and the Boston Pride Committee.

I am grateful to the many participants who served as the source of data for these studies. Without the commitment of their time, it would have been impossible to create this dissertation.

Three women, representing three generations of my family, have given me an infinite amount of love, inspiration, joy, and wisdom. I dedicate this work to my grandmother, Peggy; my aunt, Jenny; and my cousin, Madison. I love you.

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LIST OF ABBREVIATIONS

AOI	area of interest
BCR	benefits-costs-risks
CFC	chlorofluorocarbon
CFC-11	trichlorofluoromethane
CTLP	Chemical Thinking Learning Progression
FC	fixation count
FD	fixation duration
FTIR	Fourier transform infrared
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HFE	hydrofluorinated ether
IFD	individual fixation duration
LP	learning progression
MCT	mercury-cadmium-tellurium
MFC	mass flow controller
MS	mass spectroscopy
NRC	National Research Council
ODP	ozone depletion potential

ORDM	one reason decision making
PCCR	pupil centre corneal reflection
RMS	reaction modulation spectroscopy
RO	ratio of occurrence
sccm	standard cubic centimeters per minute
TFC	total fixation count
TFD	total fixation duration
UMBAR	UMass Boston Atmospheric Reactor
UV	ultraviolet
VOC	volatile organic compound

CHAPTER 1

INTRODUCTION

The status of chemistry in society is a profound dichotomy of perceptions, and neither of these perceptions are in consistent agreement with the facts.

-- Paul T. Anastas and John C. Warner[1] --

Green chemistry is a philosophy of chemistry that emphasizes a decreasing dependence on limited non-renewable resources and an increasing focus on preventing pollution byproducts of the chemical industry. In short, it is the discipline of chemistry practiced through the lens of environmental stewardship. Green chemistry is applicable to all stages of chemical synthesis, from design to manufacture. In 1998, Anastas and Warner defined twelve principles to guide chemists in their practice of the discipline:[1]

1. Prevention: It is better to prevent waste than to treat or clean up waste after it has been created.
2. Atom economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less hazardous chemical synthesis: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Designing safer chemicals: Chemical products should be designed to affect their desired function while minimizing their toxicity.
5. Safer solvents and auxiliaries: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Design for energy efficiency: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. Use of renewable feedstocks: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. Reduce derivatives: Unnecessary derivatization (use of blocking groups, protection/deprotection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. Catalysis: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for degradation: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. Real-time analysis for pollution prevention: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Inherently safer chemistry for accident prevention: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Shifting the practice of chemistry to the perspective of Anastas and Warner, the same perspective held by a growing number of chemists, is by no means an easy task, considering the history of chemistry practice. Chemists have historically concerned themselves with the advancement of science and associated technologies. In fact, chemistry has been characterized as a technoscience, blending scientific pursuits with technological applications.[2–4] The use of foundational techniques in chemistry date back to ancient history, a time of much simpler human needs: extracting metal from ore for tools and weapons, rendering fat into soaps, dyeing, glassmaking, and determining the healing properties of plants to name just a few.[2,5] Over time, chemistry has evolved with the needs of society, but chemists still aim to develop coherent accounts of natural phenomena and create processes and knowledge that can be used to extend the abilities of mankind. To that end, chemists practice the techniques of design, application, and evaluation in order to analyze, synthesize, and transform substances.[6] The purpose of green chemistry is not to alter these pursuits. It is intended to serve as a guiding light for the moral and ethical practice of chemistry.

Green Chemistry Education

For the philosophy of green chemistry to be fully realized it will be necessary for the next generation of chemists to have proper training in the ideas, techniques, and principles that are central to its understanding.[7] Not only are these practices becoming increasingly important to chemists, but they are becoming ever more imperative for the education of a scientifically literate society. Eilks and Rauch[8] argue that chemistry education has to contribute to making students capable of actively participating in society, including the capability to make informed decisions that impact both their personal lives and society as a whole. This sentiment was recently echoed in a session on green chemistry at the *2014 Biennial Conference on Chemical Education*, where speakers pointed out that the reason chemistry education needs to become inherently greener is because it is the standard that industry employers are seeking in potential employees.[9]

While some institutions have readily implemented curricula to cover chemistry through a new, greener, lens, the adoption is often evidenced in markedly different ways. Institutions that claim to have adopted green chemistry education practices vary in terms of the degree of adoption, motivation for adoption, and definition of green chemistry education.[10] For example, some universities add in a green chemistry component to a class, or add an entire stand-alone course. Others use textbooks with a green chemistry component. Some institutions employ greener laboratory practices (e.g. choosing less toxic materials, microscale, or virtual labs). However, many institutions as yet make no efforts to adapt to a green chemistry philosophy, either in education or in practice. Implementation of a green educational philosophy in many chemistry departments is hindered by a lack of teaching materials, already over-crowded curricula, and instructors who are unwilling to teach a topic with which they are unfamiliar.[11]

Despite the slow progress of adopting green chemistry educational practices, there has recently been an effort to encourage academic institutions to adopt curricula that incorporate green chemistry concepts, practices, and philosophies. The Green Chemistry Institute (GCI), once an independent organization, became part of the American Chemical Society (ACS) in 2001.[12] One of the GCI's strategic goals is to "advocate progress in education and communication of the principles of green chemistry."[12] As part of this mission the Institute provides resources for students and educators, including workshops, webinars, links to textbooks, and a list of academic programs nationwide.

Beyond Benign, a non-profit organization whose mission is to promote green educational practices via public outreach, has begun an initiative asking institutions to pledge to accelerate the adoption of greener curricular practices.[13] The initiative, termed *The Green Chemistry Commitment*, had 23 early adopters.[14] Institutions who sign the commitment are expected to have graduated chemistry majors who: (i) have a working knowledge of the twelve principles of green chemistry; (ii) have an understanding of toxicology and how molecular mechanisms can affect human health and the environment; (iii) possess the ability to assess chemical products and processes and design greener alternatives when appropriate; and (iv) be prepared to serve society in their professional capacity as scientists and professionals.[14]

The work presented in this dissertation is an effort to advance green chemistry education at the undergraduate level. It aims to provide empirical grounding for the design of greener chemistry education materials which can be taken up by institutions that will adopt greener curricular practices. Providing this empirical grounding demands an understanding of how students develop the ability to practice chemistry in greener ways. Gaining such perspective requires expertise in green chemistry as well as research that examines how students develop greener chemical thinking.

Overview and Context

This dissertation is a culmination of six years of work in two distinct sub-disciplines of chemistry: atmospheric chemistry and chemistry education. It will demonstrate a range of interests, from chemical reactions in the atmosphere to the use of modern technology to explore the ways that specific concepts of chemistry are learned.

Determination of OH-Initiated Oxidation Pathways for a Hydrofluorinated Ether

Chemistry, being concerned with both technological and scientific pursuits, includes among its aims the solving of anthropogenic problems. In these endeavors, chemists sometimes have an incomplete knowledge of potential risks. A look at the history of chlorofluorocarbons (CFCs), provides a good example. Refrigeration units were once solely commercial appliances. Their use of highly flammable and toxic gases, with ideal engineering properties, made them dangerous for household use. In the late 1920s though, chemists at the Frigidaire Corporation introduced newly discovered compounds, CFCs, which had ideal thermochemical properties for use in refrigerators without the issues of flammability and toxicity.[15] Unfortunately, those chemists did not consider the risks of widespread use of these compounds. The risks of global impact were unknown until 1974 when Molina and Rowland, two chemists, made claims about the potential risks of CFC usage[16] which spurred an effort to ban the ozone-depleting compounds in the mid- to late-1980s. They won the 1995 Nobel Prize in Chemistry for their work in atmospheric chemistry.

This history should serve as a warning for chemists to endeavor to better understand the potential impacts of their discoveries, a chief aim of green chemistry practice. To that end, the work presented in Chapter 2 of this dissertation – including a more detailed history of CFCs and their usage – has, at its core, the aim of understanding the ways in which the global use of a different refrigerant could potentially cause environmental or human health concerns.

Benefits-Costs-Risks Analysis

Chemists must rely upon their ability to analyze outcomes, make decisions and recommend actions which they feel best represent the practice of green chemistry, because it is often difficult to uphold all of the principles of green chemistry at the same time. In this dissertation, analysis of this type is referred to as benefits-costs-risks (BCR) analysis. To illustrate BCR analysis, consider the example of the work of Svante Arrhenius, a Swedish physical chemist. In 1896, Arrhenius was the first person to link changes in atmospheric carbon dioxide concentration to global climate change.[17] Although he recognized the impact of fossil fuel burning on atmospheric CO_2 levels, he estimated that it would take 3,000 years for such activity to double CO_2 concentrations.[18] In his estimation, however, global warming would result in better living conditions and higher crop yields. Perhaps because of his analysis, concern over anthropogenic climate change was delayed many decades from this initial discovery.

The success of the next generation of green chemists as environmental stewards will depend on their ability to analyze the benefits, costs, and risks and to appropriately reason about the outcomes, both intended and unintended, of their decisions. The study undertaken in Chapter 3 of this dissertation was conducted to better understand how chemists – novice through expert – develop an understanding of, and ability to perform, BCR analysis. Results of the study contributed to the construction of a learning progression on benefits-costs-risks reasoning in chemistry and have the potential to impact curricula, instructional materials, and assessments to improve the academic training of green chemists.

Structure-Property Relationships

Key to chemists being able to assess risks, as well as to project benefits and to determine costs, is the ability to predict the properties of substances, such as solubility and partitioning, based on molecular level structures and to interpret properties, such as spectra, to infer structural information. Thus, it is important to learn how students develop structure-property relationships reasoning in the context of BCR. The work presented in Chapter 4 employs the use of eye tracking, a relatively new technique in chemistry education research, to explore students' understanding of structure-property relationships in the context of infrared spectroscopy and global warming potentials of hydrocarbons and CFCs. It is hoped that this work will lead to instructional changes that help students better understand information contained in visualizations of molecular structures so that they can incorporate such information into their BCR analysis, thereby improving their skills as practicing green chemists.

Research Questions

The research presented in this dissertation proposes to answer the following research questions:

1. What are the likely pathways for the atmospheric oxidation of HFE-7100 by OH? (Chapter 2)
2. How do students reason about benefits, costs and risks in real world context that is relevant to chemistry? (Chapter 3)
3. What evolution of implicit assumptions can account for the relative degrees of sophistication of benefits-costs-risks reasoning from novice to expert? (Chapter 3)
4. What does examination of eye gaze patterns reveal about chemistry students' understanding of structure-property relationships when presented with molecular structures and infrared spectra? (Chapter 4)
5. In what ways do the understanding, interpretation, and assimilation of information in infrared spectra vary for students at different levels in their chemistry education? (Chapter 4)

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CHAPTER 2

DETERMINATION OF THE OH-INITIATED ATMOSPHERIC OXIDATION PATHWAYS FOR A HYDROFLUORINATED ETHER

We can't solve problems by using the same kind of thinking we used

when we created them.

-- Albert Einstein --

Introduction and Motivation

The earth's atmosphere is vital for the survival of its inhabitants. It provides the air we breathe, helps to maintain livable surface temperatures, and protects us from harmful radiation. Because it plays such an important role, it is equally important that we understand how it is sustained and how anthropogenic influences can alter its chemical functioning.

Countless chemical reactions are occurring in the atmosphere every second. These reactions aid in maintaining the chemical balance of the atmosphere. However, anthropogenic inputs of nitrogen, sulfur, and volatile organic compounds (VOCs) have worked to alter the chemical soup that sustains the human race.

Beginning with the Air Pollution Control Act of 1955, endeavors to understand chemical reactions in the atmosphere have been growing at an increasing pace.

Investigations in the field of atmospheric chemistry have focused on understanding atmospheric smog,[1–9] determining the fates of VOCs,[10–20] and, most recently, understanding the effects that compounds released into the atmosphere can have on the ozone layer and global climate change.[21–34]

An Overview of the Earth's Atmosphere

Earth's atmosphere is a blanket of gases surrounding the planet. Nitrogen, oxygen and argon are its primary components, making up roughly 99.9% of the composition. These gases are generally unreactive, thus the majority of the chemistry that occurs in the atmosphere is driven by the chemical species that make up the remaining 0.1%. Even though their concentration in the atmosphere is very small, radical species in the atmosphere react rapidly and are regenerated, allowing them to be large contributors to chemical reactions in the atmosphere.

Table 2-1. Globally averaged concentrations of the well-mixed chemical species in the earth's atmosphere. Concentrations are by volume. Species whose concentration is geographically dependent, such as water (0.001% to 5%), are omitted.

Species	**Chemical Formula**	**Concentration**
nitrogen	N_2	78.08%
oxygen	O_2	20.95%
argon	Ar	0.93%
carbon dioxide	CO_2	0.0365%
hydrogen	H_2	560 ppbv

Figure 2-1 shows the pressure and temperature of the atmosphere with changing altitude. The characteristic structure of the atmosphere is largely a result of temperature changes with altitude. The *troposphere* (altitude ≤15km) is the lowest level of the atmosphere. Typically, it is in the troposphere where anthropogenic pollutants get injected. It is also where they are removed via oxidation by other chemical species. At the tropopause (~15 km), the temperature dependence begins to change, with temperatures in the stratosphere rising as a result of exothermic chemical processes occurring there, causing a distinct stratification of the atmosphere. It is here that the *stratosphere* (~15 km to 50 km) begins.

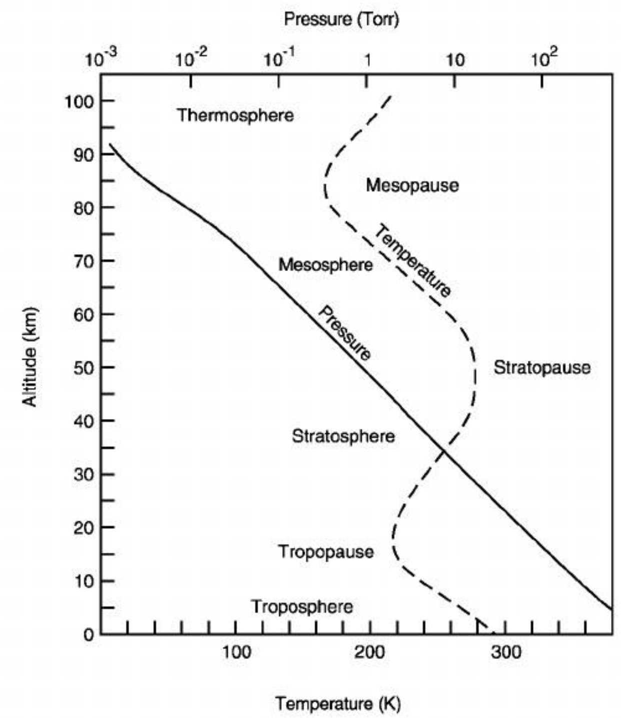


Figure 2-1. Temperature (K) and pressure (Torr) of the atmosphere at indicated altitude (km). Note that at the tropopause the temperature changes as a result of the exothermic Chapman Cycle in the stratosphere. Republished with permission of Elsevier Science & Technology Books, from Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications, by Barbara J. Finlayson-Pitts and James N. Pitts, Jr., 1999; permission conveyed through Copyright Clearance Center, Inc.

Because of the unique temperature differences, mixing between the stratosphere and troposphere across the tropopause occurs very slowly. The tropopause results in a clear delineation of the chemistry between the troposphere and the stratosphere, thus the two must be characterized separately. The change in the temperature dependence at the tropopause is a result of the Chapman cycle, a series of reactions responsible for the generation of steady-state concentrations of ozone above this altitude, a mechanism that is exothermic:

(Reaction 1) $O_2 + h\nu_{(200\text{-}240\text{nm})} \rightarrow 2O$

(Reaction 2) $O + O_2 + M^* \rightarrow O_3$

(Reaction 3) $O + O_3 \rightarrow 2O_2$

(Reaction 4) $O_3 + h\nu_{(240\text{-}310\text{nm})} \rightarrow O^* + O_2$

The ozone generated in the stratosphere is important as a means of shielding the Earth's surface from harmful UV radiation, a leading cause of skin cancer. This UV shield also restricts the photochemistry of the atmosphere to reactions that are activated at longer wavelengths.

Chemical Reactions in the Troposphere

The troposphere is a complex system of life-sustaining gases, volatile organic pollutants, numerous oxidizing agents, and products of the reactions of these ingredients with each other. Trying to understand the co-occurrence of these reactions and the co-

---

[*] M represents any chemical species capable of carrying away the energy of the reaction of O with O_2.

existence of these substances can be mind-boggling. But studies over the past half-century have helped to clarify a lot of this fog.

The removal of pollutants in the troposphere occurs via oxidation by chemical species, primarily radicals, present there. Typical tropospheric oxidants include hydroxyl radicals (OH), ozone (O_3), nitrate radicals (NO_3), hydroperoxyl radicals (HO_2), and chlorine radicals (Cl). It is generally recognized that OH and O_3 are the primary oxidants of organics in the troposphere.[35] The primary focus of the research contained here is on the oxidation by OH.

Around 1970, it was suggested that OH was the primary driving force of polluted and clean atmospheres during the daytime hours.[36–38] It was found that OH initiates chain reactions by attack on VOC or carbon monoxide (CO), forming radical species that are then propagated through further reactions, as shown in Figure 2-2.

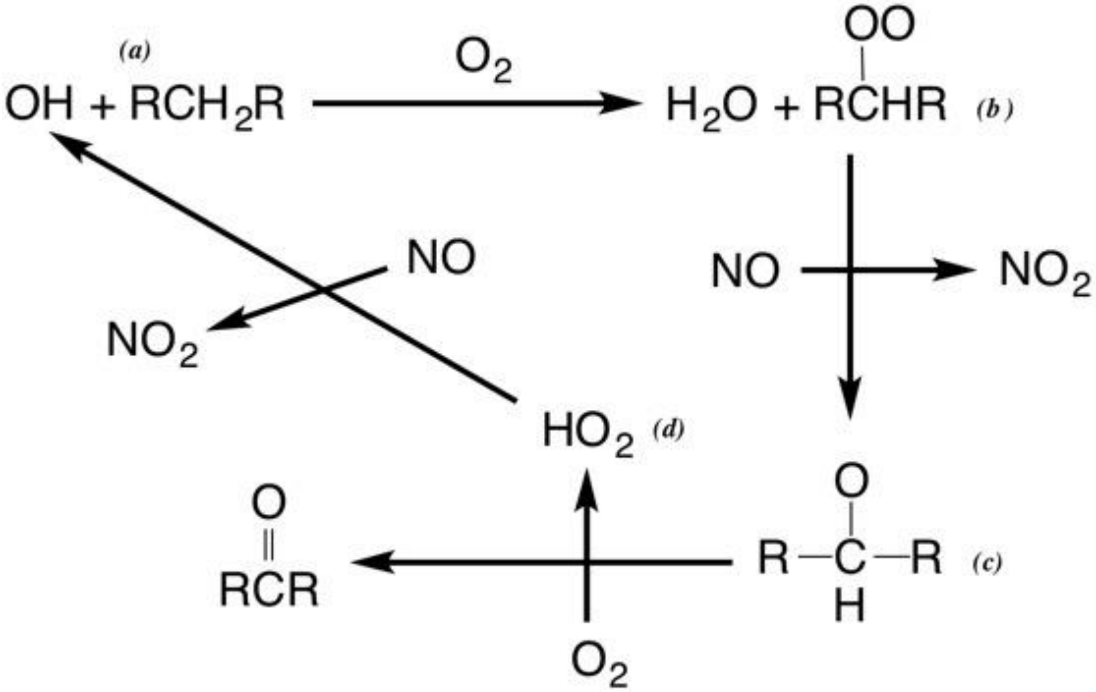


Figure 2-2. Typical sequence of elementary reactions in which OH initiates the oxidation of an alkane in the troposphere. (a) OH abstracts a hydrogen to form water and a carbon-centered radical. O_2 addition occurs at the radical site. (b) NO is oxidized to NO_2, leaving an oxygen-centered VOC radical. (c) O_2 abstracts a hydrogen to form a ketone and HO_2. (d) HO_2 is reduced by NO to reform the OH radical catalyst and NO_2. As part of this cycle, the OH is regenerated, two molecules of NO are oxidized to NO_2, and the VOC molecule is oxidized to a ketone. This is not the only possible reaction mechanism for OH with other VOCs. Republished with minor adaptations with permission of Elsevier Science & Technology Books, from *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, by Barbara J. Finlayson-Pitts and James N. Pitts, Jr., 1999; permission conveyed through Copyright Clearance Center, Inc.

Table 2-2 summarizes the fate of VOCs in the atmosphere with respect to certain OH reaction mechanisms. The research described here is focused on understanding the OH addition and abstraction mechanisms for VOCs of interest. These reactions produce additional free radicals that are capable of a continuous chain of reactions that regenerate radicals.

Table 2-2. Pathways for the removal of VOCs from the troposphere.

Property of VOC	**Mechanism**	**Result**
Water Soluble	Precipitation	Returns to the earth's surface
Photolabile at $\lambda \geq 290$nm	Photodegradation	Free radicals are produced
Multiple bonds	OH addition occurs	
Abstractable H	OH abstraction occurs	

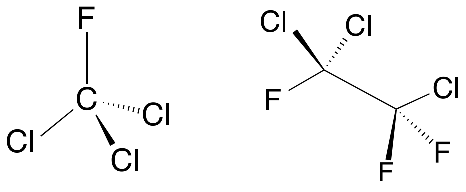
The primary source of OH in the troposphere is the reaction of singlet oxygen (formed via the photolysis of O_3) with water vapor:

(Reaction 5)

$$O + H_2O \rightarrow 2OH$$
$$k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

History and Chemistry of Refrigerants

Refrigeration units were introduced in the mid-to-late 1800s. At this time, gases such as ammonia, sulfur dioxide and methyl chloride were used in compression units in order to achieve cooler temperatures. These compounds, though ideal in their “engineering” properties, posed hazards due to their flammability and toxicity issues. Because of these risks, refrigerators were not available for household use until the late 1920s. It was during this time that the Frigidaire Corporation introduced newly discovered compounds with the desired thermochemical properties, low flammability, low toxicity, and high stability (i.e., low reactivity).[39] They had discovered chlorofluorocarbons (CFCs). As their name suggests, CFCs are compounds composed only of carbon, chlorine, and fluorine. Some representative examples are shown in Figure 2-3.



(a) (b)

Figure 2-3. Representative CFC compounds: (a) CFC-11 (i.e. trichlorofluoromethane) and (b) CFC-113 (*i.e.*, 1,1,2-trichlorotrifluoroethane). A numbering system is used to name fluorinated alkanes, prefixed with CFC or HCFC. The last value indicates the number of fluorine atoms, the next value to the left indicates the number of hydrogen atoms plus one, and the next value to the left is the number of carbon atoms less one.

CFCs made refrigeration units a highly commercial technology. With their growing use, however, the questions of their environmental impacts also grew. In 1974, Molina and Rowland[40] published the first indication that CFCs could prove detrimental on a global scale, work which was recognized with the Nobel Prize in Chemistry in 1995. They theorized that the release of CFCs into the atmosphere could lead to stratospheric ozone depletion, but without satellite data to support their claims, they could provide little experimental evidence for an argument to discontinue the use of CFCs. However, in the 1980s, the launch of satellites capable of monitoring stratospheric ozone finally supported their claims by showing ozone-depleted regions in the atmosphere. Figure 2-4 shows a satellite image of the Antarctic stratospheric ozone hole from the Total Ozone Mapping Spectrometer taken on September 16, 1987.

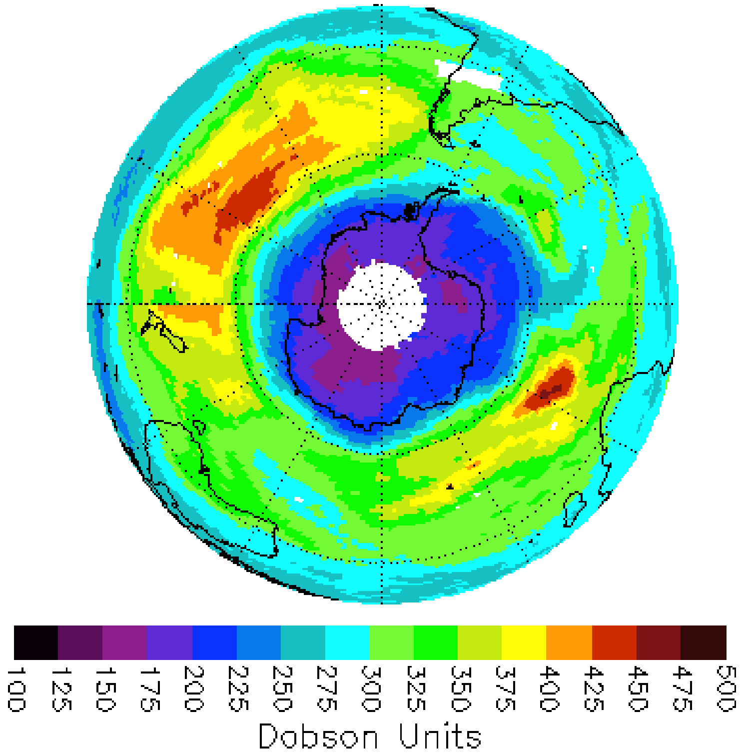


Figure 2-4. Total Ozone Mapping Spectrometer (TOMS) Satellite image of the Antarctic stratospheric ozone hole for September 16, 1987. Stratospheric ozone is measured in Dobson Units (DU), which is the number of molecules required to create a layer of pure ozone 0.01 mm thick at a temperature of 0 ºC and a pressure of 1 atm. The average amount of ozone in Earth's atmosphere is 300 DU. *Image credit: http://ozoneaq.gsfc.nasa.gov/NIMIMGSP1987.md*

The unreactive nature of CFCs makes them the ideal candidates for their intended use, but this stability means that they are immune to reactions with OH and NO_3 in the troposphere that are the typical pathways for scrubbing VOCs (see, for example, Table 2-2). The research described here is focused on understanding the OH addition and abstraction mechanisms for VOCs of interest. These reactions produce additional free radicals that are capable of a continuous chain of reactions that regenerate radicals.

Thus, CFCs are easily, albeit slowly, transported into the stratosphere. It is here that the wavelength distribution of solar radiation shifts to shorter, higher energy wavelengths; wavelengths that are capable of dissociating the carbon-chlorine bonds (76 kJ mol^{-1} dissociation energy)[35] within the molecule. For example, the photolytic degradation of CFC-12 in the stratosphere is:

(Reaction 6) $CF_2Cl_2 + h\nu\ (\lambda<240\text{nm}) \rightarrow CF_2Cl + Cl$

This release of chlorine radicals directly into the stratosphere is problematic for the once chemically stable environment. Chlorine radicals catalyze the depletion of ozone by:

(Reaction 7) $Cl + O_3 \rightarrow ClO + O_2$

(Reaction 8) $ClO + O \rightarrow Cl + O_2$

The net reaction of which is:

(Reaction 9) $O_3 + O \rightarrow 2O_2$

This catalytic cycle occurs predominantly in the mid and upper stratosphere, where the concentration of oxygen atoms is highest as a result of the Chapman Cycle (Reactions 1 through 3 above). In the lower stratosphere, higher concentrations of hydroxyl and hydroperoxyl radicals from the troposphere alter the method of ozone depletion by chlorine radicals:

(Reaction 10) $Cl + O_3 \rightarrow ClO + O_2$

(Reaction 11) $ClO + HO_2 \rightarrow HOCl + O_2$

(Reaction 12) $HOCl + h\nu \rightarrow Cl + OH$

(Reaction 13) $OH + O_3 \rightarrow HO_2 + O_2$

The net reaction of which is:

(Reaction 14) $2O_3 \rightarrow 3O_2$

In reactions 9 and 14, Cl is a catalyst, and remains free in the stratosphere. Thus, a single chlorine radical can continue on to destroy more ozone. Furthermore, this is the reaction pathway of *only one* of the Cl atoms in a single CFC molecule, which contains multiple chlorines and which were released into the atmosphere at an international scale.

In 1985, 20 nations convened at the Vienna Convention to begin talks on ozone-depleting substances. The product of their work was the Montreal Protocol on Substances that Deplete the Ozone Layer, agreed upon by the convention's participating nations in September, 1987, and entered into force the first day of 1989. The Protocol required that CFCs be phased out completely in a step-wise fashion by 1996. To be feasible, though, it was necessary to find a suitable replacement for CFCs. Hydrochlorofluorocarbons (HCFCs) were also in use at the time, and because of their lower chlorine content, they were used as a temporary substitute.

HCFCs are a class of compounds that are structurally similar to CFCs. Some representative examples are shown in Figure 2-5. They differ from CFCs in that they contain hydrogen in addition to the carbon, chlorine, and fluorine contained in CFCs. HCFCs are less damaging to ozone than CFCs because of their hydrogen-substituted nature. Their increased hydrogen content makes it possible for HCFCs to be partially removed in the troposphere by hydroxyl radical (OH) oxidation pathways (refer to Table 2-2), but a fraction of the chlorine-containing molecules still reaches the stratosphere and ozone-destruction reactions are able to proceed. Because of their chlorine content, HCFCs are not a suitable permanent replacement and were scheduled to be phased out completely according to the Montreal Protocol by 2030. As HCFCs continue to be phased out, there is a growing need for viable alternatives that are suitable for the current infrastructure that uses them.

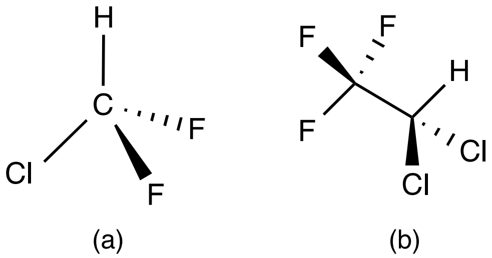


Figure 2-5. Representative HCFC compounds: (a) HCFC-22 (i.e. chlorodifluoromethane) and (b) HCFC-123 (i.e. 2,2-dichloro-1,1,1-trifluoroethane). A numbering system is used to name fluorinated alkanes, prefixed with CFC or HCFC. The last value indicates the number of fluorine atoms, the next value to the left indicates the number of hydrogen atoms plus one, and the next value to the left is the number of carbon atoms less one.

Hydrofluorocarbons (HFCs) make a somewhat better alternative than HCFCs. With no chlorine atoms present in their structure, they have no significant impact on stratospheric ozone concentrations.[†] HFCs such as HFC-134a are already being used in household refrigerator/freezer systems without the need for an HCFC intermediate. [21] Because of the increased hydrogen content of HFCs, they are easily degraded by typical tropospheric degradation mechanisms (refer to Table 2-2). For example, the degradation of HFC-134a proceeds by:

(Reaction 15) $CF_3CH_2F + OH \rightarrow CF_3CHF + H_2O$

(Reaction 16) $CF_3CHF + O_2 \rightarrow CF_3CHFO_2$

(Reaction 17) $CF_3CHFO_2 + NO \rightarrow CF_3CHFO + NO_2$

[†] Fluorine atoms, which are also capable of destroying ozone, are rapidly converted to hydrofluoric acid (HF) in the atmosphere. HF is a stable reservoir and prevents fluorine from contributing to ozone depletion to any significant degree.

(Reaction 18) $CF_3CHFO + O_2 \rightarrow CF_3COF + HO_2$

For wet deposition, the lifetime of CF_3COF is on the order of days.[22] The major product of hydrolysis, though, is $CF_3C(O)OH$, known as trifluoroacetic acid (TFA), which has been speculated to inhibit growth of terrestrial and aquatic flora. This concern, coupled with the fact that HFCs have high potential to impact global climate forcing (see “Radiative Forcing and Global Warming Potential” below), means that HFCs are not an ideal replacement.

Now knowing that these compounds have a widespread, and long-lasting, global impact on chemical processes in the atmosphere, it is important for society to understand the potential impacts of any new substitutes before their introduction.

Ozone Depletion Potential

Knowing that certain compounds can lead to stratospheric ozone depletion necessitates simple measures for comparing their different impacts on ozone as scientific guidelines for policy-making.[41] Use of a calculable "ozone depletion potential" (ODP) has been proposed as a simple scale for quantifying the effects that various compounds can have on stratospheric ozone.[41–43] In 1992, a semi-empirical approach was developed and applied to the estimation of ODPs on both short and long time scales. The ODP of a halogenated compound, X, is calculated by:[44]

(Equation 1) $$ODP_x(t) = \left(\frac{F_x}{F_{CFC-11}}\right)\left(\frac{M_{CFC-11}}{M_x}\right)\left(\frac{n_x}{3}\right)\alpha\left(\frac{\int_{t_s}^{t} e^{-\frac{t-t_s}{\tau_x}}\,dt}{\int_{t_s}^{t} e^{-\frac{t-t_s}{\tau_{CFC-11}}}\,dt}\right)$$

The ratio $F_x/F_{CFC\text{-}11}$ is the fraction of the compound that has been dissociated in the stratosphere compared to that of CFC-11. Both of these fractions are obtained from measurements. The terms M and τ indicate the molecular weights and atmospheric lifetimes, respectively, of the indicated compounds. The term n_x is the number of chlorine or bromine atoms in the molecule (which is divided by three, the number of chlorine atoms in CFC-11). Alpha is an enhancement factor reflecting the higher efficiency with which bromine can destroy ozone molecules. The time, t_s, represents the length of time necessary to transport a molecule from the surface to the stratosphere and t represents the total time. Thus, the quantity $(t - t_s)$ represents the amount of time that the compound is available in the stratosphere for conversion into active forms of chlorine. The atmospheric lifetimes of the respective compounds are denoted by τ. Because it is used as a reference compound, CFC-11 has an ODP of 1. Compounds that do not contain chlorine (or bromine) have an ODP of zero. Table 2-3 lists the ODP of three representative CFCs and CFC replacements.

Table 2-3. Ozone depletion potentials of three representative CFCs and CFC replacement compounds.

Compound	**Formula**	**ODP**[44]*
CFC-113	$CF_2ClCFCl_2$	0.59
HCFC-22	$CHClF_2$	0.14
HFC-125	CF_3CHF_2	0.0[41]

**for a 20 year time horizon*

Radiative Forcing and Global Warming Potential

The radiative forcing of the earth's atmosphere is responsible for maintaining livable temperatures on the surface. Radiative forcing is defined as the difference between the energy received by the earth from the sun (i.e. solar radiation) and the energy radiated back to space by the earth (primarily infrared radiation). Species that produce a positive radiative forcing warm the earth because they absorb infrared (IR) radiation and re-radiate the energy, a large portion of which is redirected back to the earth's surface. It is often referred to as the greenhouse effect[‡] based on the imperfect analogy that this is how a greenhouse works. Figure 2-6 shows a simplified schematic representation of the greenhouse effect.

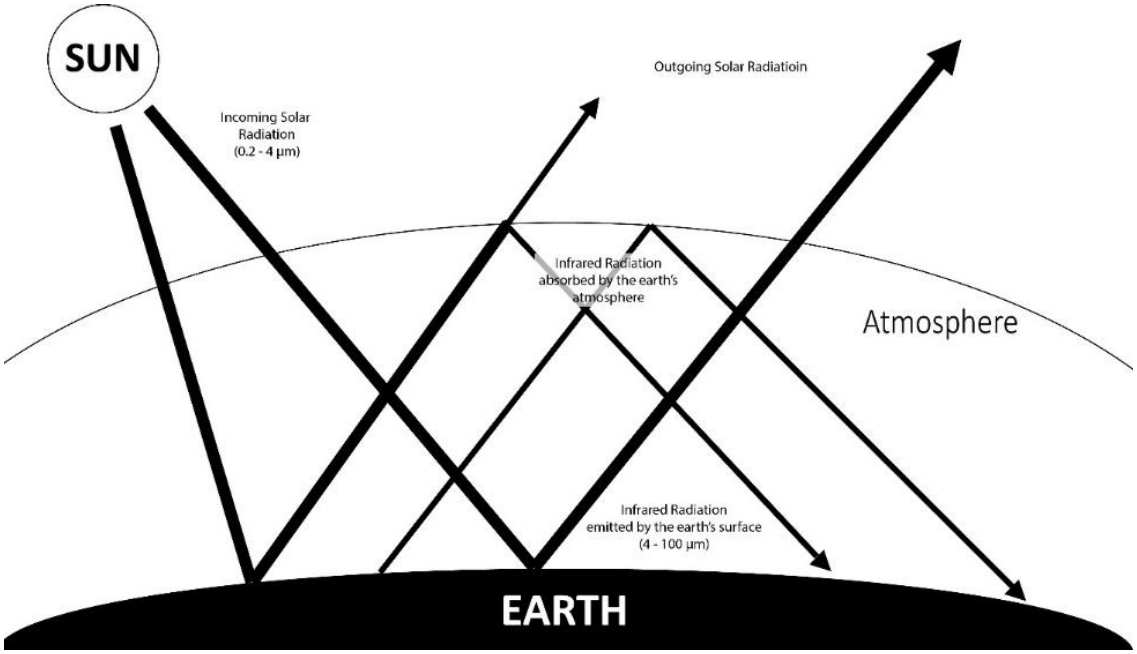


Figure 2-6. Simplified schematic representation of the greenhouse effect. Solar radiation reaching the earth's atmosphere has wavelengths of 0.2 to 4 μm. Some of the radiation is blocked by atmospheric chemical species (notably, O_3 in the stratosphere absorbs UV radiation). Some of the radiation passes through the atmosphere and warms the earth's surface. The earth, in turn, radiates energy at longer wavelengths (4 – 100 μm) which correspond to infrared radiation (i.e. heat). The infrared radiation gets absorbed and re-radiated to the earth's surface by chemical species in the atmosphere (e.g., CO_2, H_2O).

[‡] It should be noted that this is not an entirely accurate moniker as greenhouses retain heat in a fundamentally different fashion.

Energy absorption is a concentration-dependent characteristic, so any change to the concentrations of atmospheric gases causes an increase in radiative forcing. This is especially true for compounds whose maximum IR absorbance occurs in a range not previously absorbed by the natural species in the atmosphere. In other words, increased concentrations of IR-active trace gases, particularly those that absorb in the relatively clean atmospheric window from 7 to 13 µm where CO_2, H_2O, and O_3 do not absorb strongly[35] will cause an effective increase to the net energy absorbed by the troposphere, leading to a net increase in temperature. Figure 2-7 shows the IR window of the atmosphere resulting from naturally-occurring chemical species. As a result, anthropogenic releases of IR-absorbing atmospheric species, or increased emissions of traditional greenhouse gases, cause additional trapping of IR radiation.

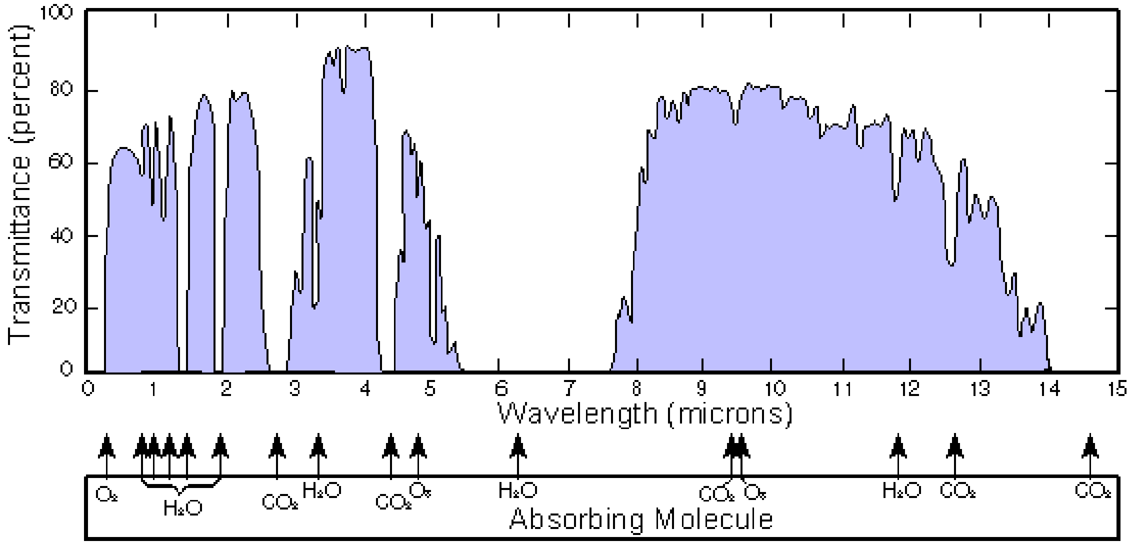


Figure 2-7. Transmittance of solar radiation through the earth's atmosphere as a function of wavelength. IR radiation is transmitted in the shaded region. Observe the increased transmittance in the 8 to 13 µm range. This region is often referred to the atmospheric window. *This figure is reproduced from an online source, http://en.wikipedia.org/wiki/Infrared_window, and is considered part of the public domain under the terms of Title 17, Chapter 1, Section 105 of the US Code.*

Not only is the IR activity of the atmospheric species important, but its lifetime in the atmosphere also affects its contribution to rising temperatures. Long-lived species, for example, make a larger contribution than short-lived species when integrated over time. Thus, a long-lived species with a strong absorption cross-section can have a drastic impact on global temperatures, even in relatively small amounts.

Thus, the effects of greenhouse gases depend on their ability to absorb IR radiation as well as their lifetime in the atmosphere. Global warming potentials (GWP) are a method of expressing the time-integrated radiative forcing due to the instantaneous emission of a fixed amount of a particular substance.[35] GWPs can be expressed both absolutely and relatively. Typically, GWP is represented relative to that of CO_2, whose GWP is defined to be 1. Relative GWP is calculated by:[35]

$$\text{(Equation 2)} \qquad \text{Relative GWP} = \frac{\int_0^{TH} a_{\text{gas}}[\text{gas}]_t \, dt}{\int_0^{TH} a_{\text{ref}}[\text{ref}]_t \, dt}$$

where [gas] represents the time-dependent concentration of the gas of interest, [ref] represents the time-dependent concentration of a reference gas (most often CO_2), and a_{x} represents the time-dependent radiative forcing of the gas or reference per unit increase in their atmospheric concentrations.

Hydrofluorinated Ethers as Potential CFC Replacements

As discussed above, CFCs, HCFCs, and HFCs have the potential to cause lasting damage to the environment. CFCs have been shown to cause stratospheric ozone destruction, a hazard to human life. While HCFCs have a higher atmospheric reactivity, and thus have the potential to be removed in the troposphere before reaching the stratosphere, their ODP is not zero. HFCs strongly addressed the ozone depletion problem because they contain no chlorine. However, it has been shown that atmospheric oxidation processes result in products that return to the earth via wet deposition, where they can have a lasting impact on terrestrial and aquatic flora. A hopeful long term solution that is currently being considered is a class of compounds known as hyrdrofluorinated ethers (HFEs). HFEs hold promise as replacements for CFCs because they have an ODP of zero and their GWPs have been shown to be much lower than those of CFCs.[45,46]

The work represented in this dissertation examined the HFE compound $C_4F_9OCH_3$ (HFE-7100) whose structure is shown in Figure 2-8. Research focused on determining the OH-initiated atmospheric oxidation products of these HFEs using the UMass Boston Atmospheric Reactor (UMBAR).

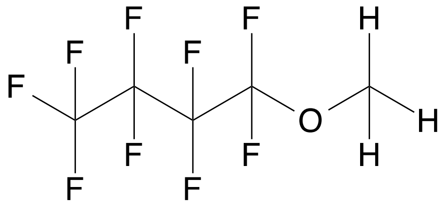


Figure 2-8. Structure of HFE-7100.

Previous work has been done which has studied the temperature dependence of the kinetics of the OH radical oxidation reactions[45–48] and the kinetics of the reaction of this HFE with Cl atoms.[49] The atmospheric lifetime was studied by Bravo *et al.*[47] and determined to range from 0.91 to 4.8 years. While this molecule is certainly less hazardous to the ozone in the stratosphere and potentially less hazardous to global climate, an in depth look at its OH-initiated atmospheric oxidation products, which have the potential to present other hazards, has yet to be conducted.

The products of OH-initiated oxidation of this HFE have not been studied, but results may prove to be similar to the Cl-initiated oxidation of HFE-7200 (as studied by Christensen *et al.*[45]) or F-substituted products of OH-initiated oxidation of ethers (as studied by Wallington and Japar[50], Nash and Francisco[51], and Espada and Shepson[52]).

Methodology

UMass Boston Atmospheric Reactor

Experiments were carried out on the UMass Boston Atmospheric Reactor (UMBAR; Figure 2-9). This reactor is a continuous flow cylindrical steel tube 4.85 m long with a 12.4 cm interior diameter. Additionally, attached to the flow reactor are mass flow controllers (MFCs), a Baratron pressure gauge, and a multi-pass infrared spectrophotometer.

UMBAR is comprised of four primary regions, as shown below: gas source region, radical source region, detector region, and sink region.

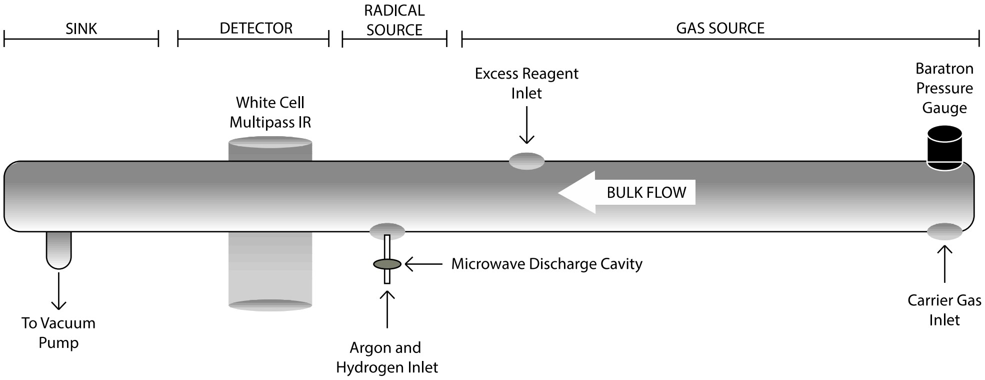


Figure 2-9. Schematic diagram of the UMass Boston Atmospheric Reactor (UMBAR).

Gas Source Region

The bulk flow originates at the upstream end of the reactor. Carrier gas is delivered via one-quarter inch diameter tubing. A 10,000 sccm MKS General Purpose Mass-Flow Controller regulates the flow of carrier gas.

The reagent of interest is introduced downstream of the carrier gas, but far enough upstream from the radical source to ensure complete mixing with the carrier gas in the flow tube before reaching the region where the reaction is expected to occur.

Near the same location as the reagent of interest, NO is introduced (and immediately oxidized to NO_2) to simulate a polluted atmosphere and also to assist with radical production further downstream.

Radical Source Region

More than two meters downstream of the carrier gas inlet is the radical injector. A quartz tube allows flow of the radicals through a microwave discharge cavity and directly to the centerline of the flow tube.

The radical source consists of a multi-component system that provides the gases (Ar and H_2) and energy (microwaves) to make the radicals. The radical source itself is an argon plasma sustained by microwave energy. The plasma is initiated within the microwave discharge cavity, attached to a Scintillonics Model HV15A microwave generator. The microwave energy entering the cavity is 22W. MKS flow controllers regulate the flow of argon and hydrogen gases into the radical source.

When the radical source is on, a series of reactions is initiated that leads to the desired OH radical in Reaction 21.

Reaction 19	$H_2 + \mu w \rightarrow 2H$
Reaction 20	$H + O_2 \rightarrow HO_2$
Reaction 21	$HO_2 + NO \rightarrow OH + NO_2$
Reaction 22	$NO_2 + OH \rightarrow HONO_2$

In Reaction 19, H_2 is dissociated in the argon plasma stream and enters the flow reactor, where the H radicals react with O_2 in the carrier gas to continue the radical chain reactions (Reaction 20, Reaction 21, and Reaction 22). The OH radicals are then able to interact with the excess reagent. Reaction 22 is an undesirable sink of OH, thus an excess of the reagent of interest is used in order to ensure that most of the OH reacts with the target molecule. Typical OH concentrations are on the order of 10^{12} molecules cm^{-3}. This concentration is roughly double the concentration of atmospheric conditions, ensuring that the chemistry occurs fast enough to be observed. When the radical source is off, there is no hydrogen flowing through the microwave discharge cavity, effectively shutting off production of all radicals (see Reaction Modulation Spectroscopy below). Although the argon flow remains the same, the plasma cannot create radicals in the absence of hydrogen.

Detector Region

The detector region consists of an infrared multi-pass White cell that is 0.6 m downstream of the radical injection site. The cylindrical White cell (Figure 2-10) is perpendicular to the main flow tube and has a diameter slightly larger than that of the main tube. The White cell is coupled to a Mattson Fourier Transform Infrared (FTIR) Spectrophotometer. The FTIR, which is external to the flow tube, sends an infrared beam out the external aperture and is redirected into the potassium bromide (KBr) entrance window on the underside of the White cell by a gold-plated mirror (labeled “F-matching transfer optics” in Figure 2-10). Once inside the cell, the beam is reflected through multiple passes by three gold-plated mirrors. The beam is then directed at an external KBr window, also on the underside of the White-cell, and finally redirected to a detector by another gold-plated mirror. The detector is a mercury-cadmium-tellurium (MCT) detector cooled by liquid nitrogen.

Sink Region

The carrier gas and other associated chemical species continue flowing past the detector region until they reach the end of the flow tube. Once there, they flow into a flexible circumferentially corrugated metal sidearm connected to a Sogevac vacuum pump, where the gas continues into a PVC waste pipe and exits the building via the building's laboratory exhaust system.

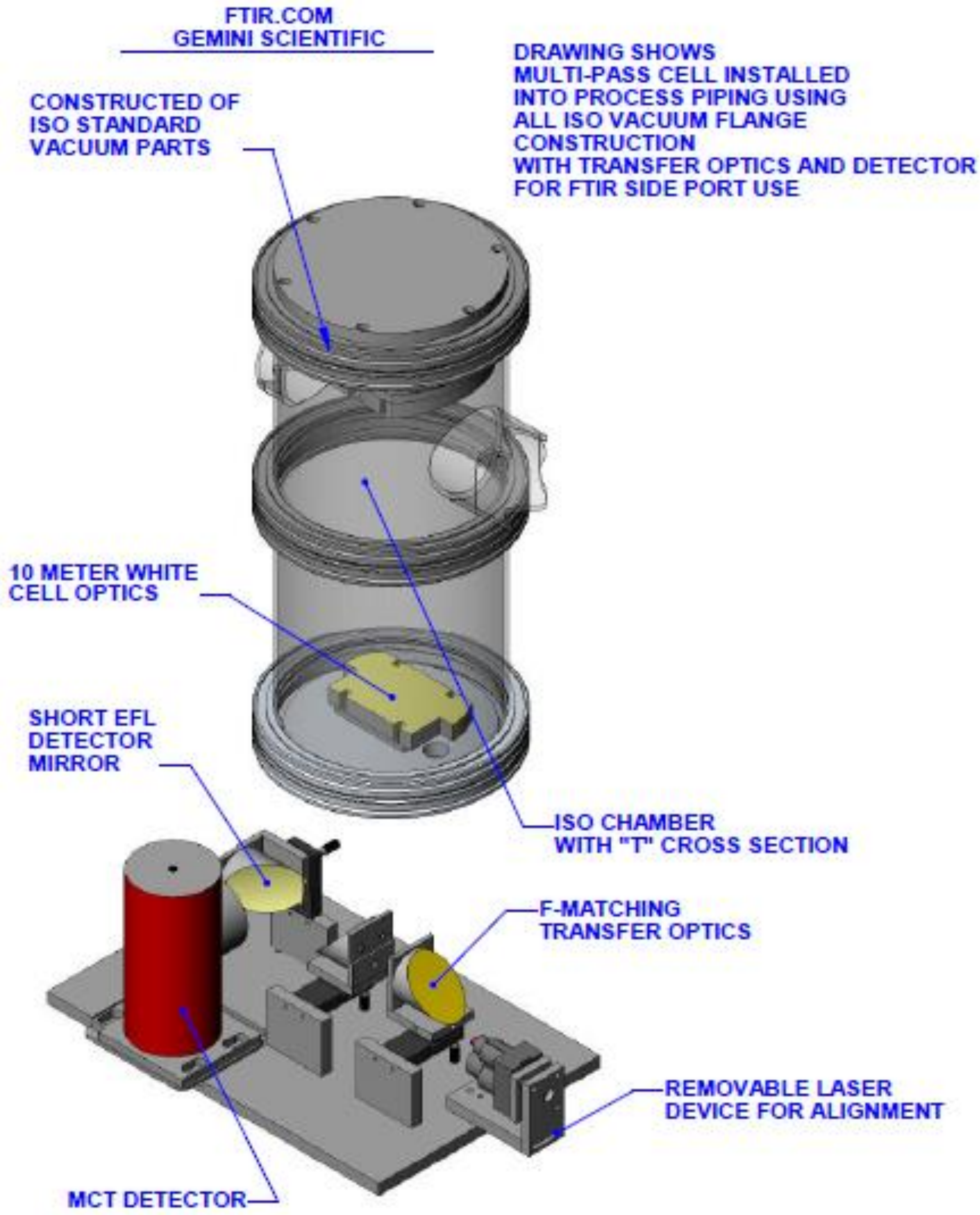


Figure 2-10. Schematic diagram of the White cell found in UMBAR's detector region. The infrared beam from the FTIR enters from the location of the removable laser device and is reflected up into the White cell at the F-matching transfer optics. The beam is reflected through multiple passes via the White cell optics mounted on the upper and lower plates and then exits the White cell to the short EFL detector mirror. This mirror redirects the beam into the MCT detector to provide the signal.

Reaction Modulation Spectroscopy

Work on UMBAR uses a reaction modulation spectroscopy (RMS) method that was first described by Donahue et al.[53] In this type of experiment, the reactor has a continuous flow of carrier gas, excess reagent, and argon. The H_2, which is used to produce radicals in the reactor, is toggled on (for an online scan) and off (for an offline scan). Thus, offline scans show a full concentration of injected excess reagent and carrier flow. Conversely, online scans show the products of the reaction of the excess reagent with the generated radicals. Two offline spectra surround an online spectrum. The offline spectra are averaged to produce a background spectrum and a ratio of the background spectrum to the online spectrum generates a transmittance spectrum that shows changes in absorption that are directly caused by the modulation of radicals. In the transmittance spectrum, peaks with higher absorption represent products formed in the presence of radicals. Peaks with lower absorption represent chemical species that are consumed in the presence of radicals.

Chemical Experimentation and Results

Work proceeded by first examining the literature to identify a theoretical OH-initiated oxidation pathway for the molecule of interest. Next, an FTIR calibration curve was generated. Finally, experimentation in UMBAR was conducted with the intent to identify reaction products.

Theoretical OH-Initiated Oxidation Pathway of HFE-7100

Based on the work of Wallington et al.[54] and Chen et al.,[46] an oxidation scheme was proposed (Figure 2-11) for HFE-7100. These works focused primarily on the reaction *kinetics* of OH-initiated oxidation of HFE-7100. In addition, they differ from this dissertation in that those studies were carried out in smog chamber apparatuses.

As can be seen in this figure, the primary reservoir species that were observed by the oxidation of HFE-7100 in smog chamber experiments are COF_2, CO_2, CH_2O, and $CF_3(CF_2)_3OC(O)H$ (indicated by solid boxes in the figure).[46,54] However, it is important to note that reactions carried out in UMBAR are sensitive to very short timescales. The experimental design was developed in such a way that first generation products would be seen, allowing for determination of the most likely pathway of OH-initiated oxidation. Alternatively, a smog chamber apparatus can be used to study products of atmospheric oxidation that occur after hours or days. These products would likely not be the first generation products that were the focus of the work presented here. Thus, for the purposes of this work, a flow style system (i.e., UMBAR) provided the best means to study the HFE + OH reaction.

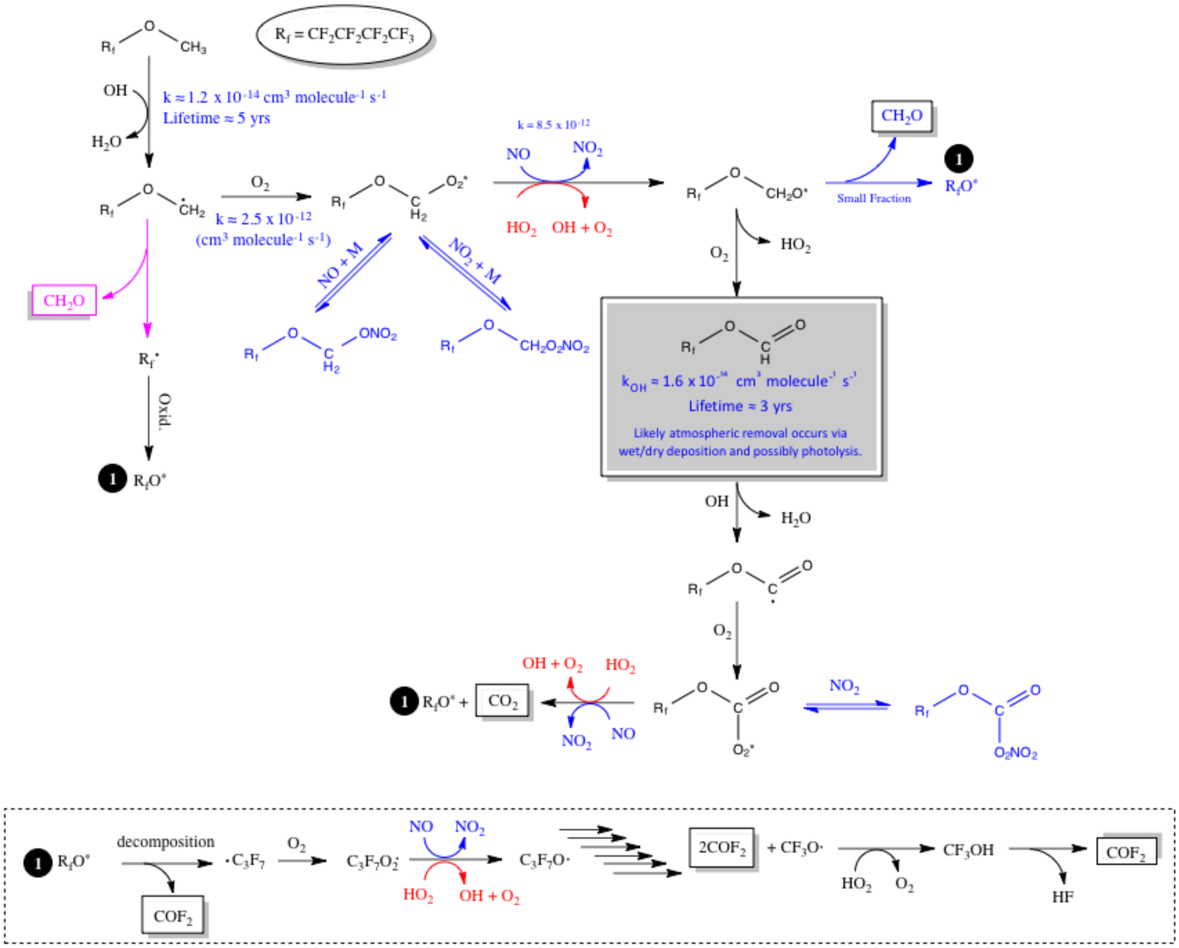


Figure 2-11. Theoretical OH-initiated oxidation scheme of HFE-7100. Information in blue was obtained from Wallington et al.[54] and information in red was obtained from Chen et al.[46] Long-lived molecular species that were observed in the IR by these authors are indicated by solid boxes.

Generation of IR Reference Cross-Sections and Calibrations

In order to run RMS subtractions for HFE chemical reactions with OH, it was first necessary to create reference spectra. Reference spectra are cross-sections of the IR absorbance for each compound at a known concentration. Because the IR pathlength of the flow tube system is poorly constrained, it was necessary to create cross-sections for the reference spectra in a cell with known pathlength (b = 10 cm) external to the UMBAR flow system.

Gaussian 09 Analysis

Gaussian 09 is a chemistry modeling software, built on the fundamental laws of quantum mechanics, that predicts energies, molecular structures, vibrational frequencies and molecular properties of molecules.[55] In this work, Gaussian 09 analysis was run for the HFE-7100 molecule in order to determine the vibrational modes that were responsible for the observed peaks in the IR cross sections. Peaks observed in the IR were assigned based on Silverstein et al.[56] and compared to the visualized vibrational motions from the Gaussian 09 programming suite.

Infrared Cross-Sections

A bulb of HFE-7100 was prepared via a glass manifold. HFE-7100 vapor was obtained by vacuum from a liquid sample. As a proxy for concentration, pressure was used to obtain number density of the gas. A 10 L glass bulb was pumped down to vacuum and filled with 20.1 Torr of HFE-7100. The bulb was then pressurized to 985.9 Torr with N_2. Using this bulb, an IR cell with a pathlength of 10 cm was pressurized to 247.7 Torr, resulting in a concentration of of 3.57 x 10^{15} molecules cm^{-3} HFE-7100.

To generate a transmittance spectrum of HFE-7100, two offline spectra (P_{cell}=0 Torr) were obtained with one online spectrum (P_{cell}=247.7 Torr) taken between them. The spectra were the result of 1000 co-added IR scans. The offline and online spectra were used to generate a transmittance spectrum of HFE-7100 via RMS analysis (see Section 2.2.2 above). The transmittance spectrum, shown in Figure 2-12, was sufficient to use for the two strongly absorbing bands, 800 cm^{-1} to 1100 cm^{-1} (band 1.1) and 1050 cm^{-1} to

1400 cm^{-1} (band 1.2). Band 1.1 is the result of several overlapping absorbances. Isolation of individual peaks in band 1.1 was impossible because the peaks were not clearly resolved in the spectrum. The first two peaks in this band were isolated in a subsequent reference cross-section (see Figure 2-13). The triplet peak that begins just below 1000 cm^{-1} is a result of an asymmetric C–O–C stretch. This supposition was confirmed by Gaussian analysis. The asymmetric stretch of C–O–C typically occurs in the range of 1085-1150 cm^{-1}.[56][§] Based on the highly electronegative nature of the nonafluorobutane ($CF_3CF_2CF_2CF_2$–) group on one side of the molecule, it is likely that the energy required to induce dipoles for the asymmetric stretch of C–O–C is lessened. The complementary symmetric C–O–C stretch is a weak absorber and is more readily observed using Raman techniques[56] which were not available for this work.

[§] Spectral peaks were assigned with the help of Silverstein et al.[61] and confirmed by analysis with Gaussian 09[60].

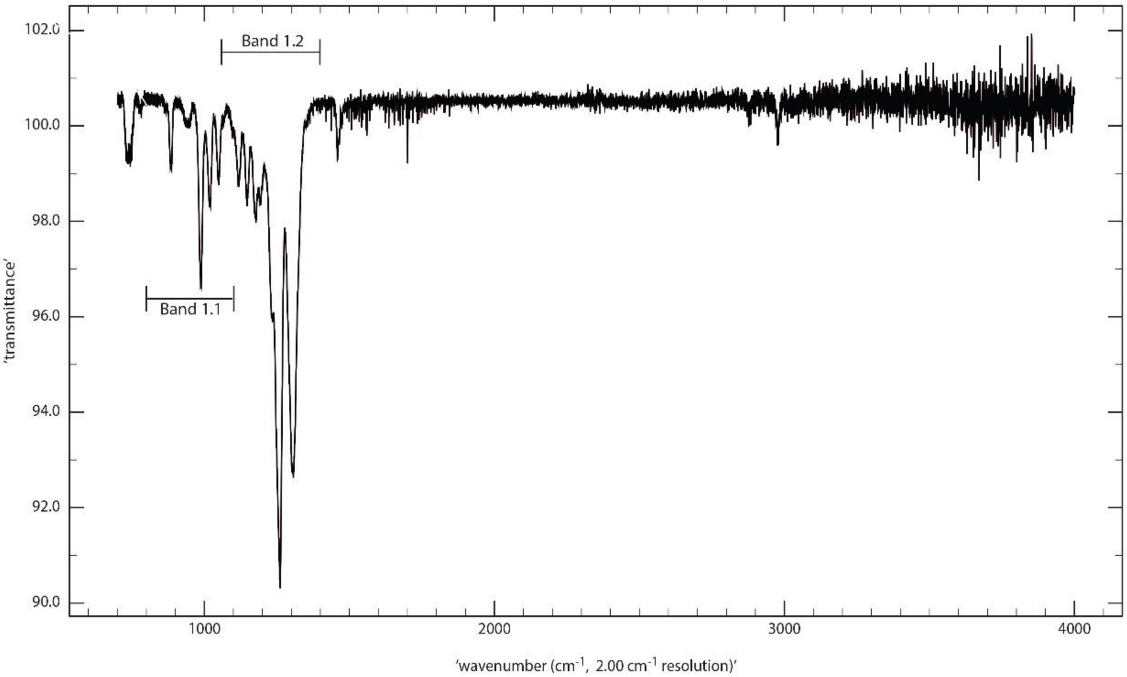


Figure 2-12. Reference spectrum one for HFE-7100. Band 1.1 encompasses 800 cm^{-1} to 1100 cm^{-1}. Band 1.2 encompasses 1050 cm^{-1} to 1400 cm^{-1}. [HFE-7100] = 3.57 x 10^{15} molecules cm^{-3}.

Band 1.2 occurs because of C–F stretching in the molecule. Carbon–fluorine bonds are known to absorb strongly in the range of 1000-1400 cm^{-1}. As the number of fluorine atoms in an aliphatic molecule increases, the number and complexity of the peaks increases.

For OH-oxidation chemistry runs, it was expected that the C–F bonds would be highly unreactive and the nature of OH-oxidation of ether bonds is not well studied. For these reasons, it was necessary to identify reference peaks for the $–CH_3$ group of the molecule. While these peaks can be seen in Figure 2-12, their signal-to-noise ratio was very low and their absorbance was not ideal (less than 1%), thus it was necessary to create an additional reference cross-section to obtain sufficient absorbance values.

Reference spectrum two, shown in Figure 2-13, used a concentration of 1.05 x 10^{16} molecules/cm^3, an order of magnitude larger than that of reference spectrum one. Four distinct bands (and one combined band) were isolated in this cross-section. While bands 2.1 and 2.2 were accounted for in a combined band of reference one (band 1.1), they were more clearly resolved in this cross-section. Based on Gaussian 09 results, band 2.1 is the result of complex F–C–F bending while band 2.2 occurs because of a stretch involving C–O–C and C–F. Bands 2.3 (1440-1490 cm^{-1}), 2.5 (2863-2888 cm^{-1}), and 2.6 (2957-2989 cm^{-1}) are results of the bending and stretching modes within the CH_3 group of the molecule. Band 2.4 (2863-2989 cm^{-1}) is a combination of bands 2.5 and 2.6.

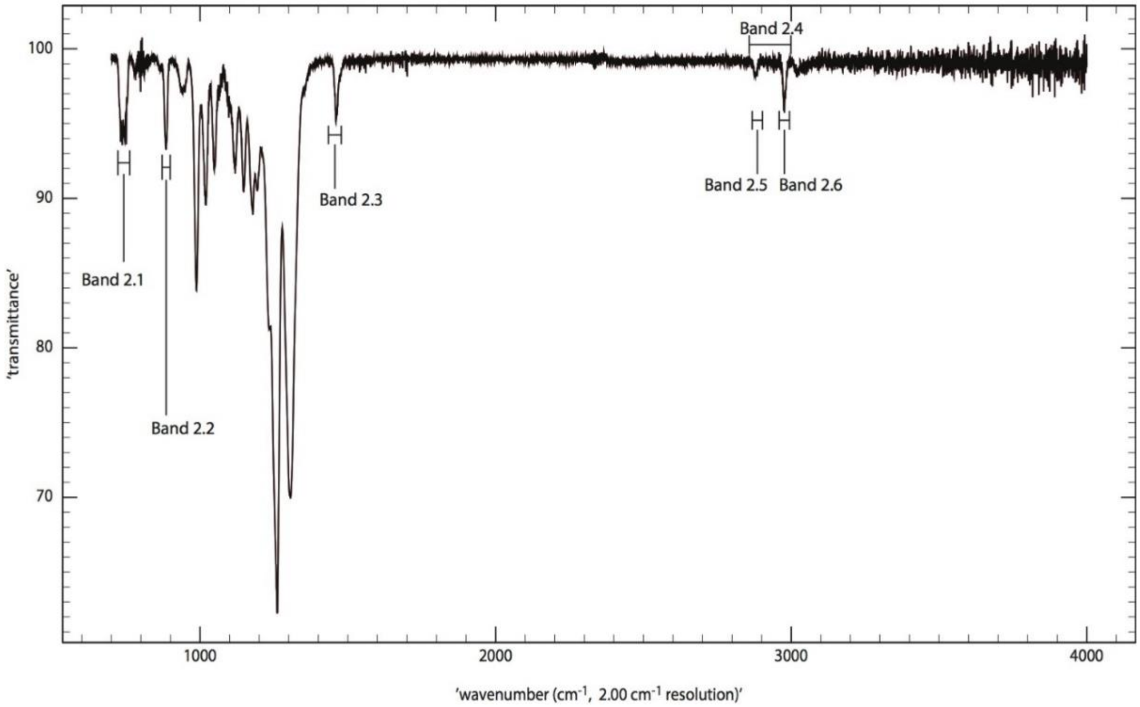


Figure 2-13. Reference spectrum two for HFE-7100. Band 2.1 encompasses 720 cm^{-1} to 760 cm^{-1}. Band 2.2 encompasses 870 cm^{-1} to 900 cm^{-1}. Band 2.3 encompasses 1440 cm^{-1} to 1490 cm^{-1}. Band 2.4 encompasses 2863 cm^{-1} to 2989 cm^{-1}. Band 2.5 encompasses 2863 cm^{-1} to 2888 cm^{-1}. Band 2.6 encompasses 2957 cm^{-1} to 2989 cm^{-1}.

Absorbance at 1450 cm^{-1} (band 2.3) is a known out-of-phase (asymmetrical) bending of the C–H bonds within the methyl group. The complimentary symmetrical bending typically occurs at 1375 cm^{-1}. However, that region of the spectrum is dominated by the very strong absorbance resulting from multiple C–F stretching modes in the molecule. Upon close inspection, it is possible to see a shoulder of a small peak that occurs at the tail end of band 1.2. It is highly likely that this shoulder is the result of symmetrical bending of the C–H bonds of CH_3.

Bands 2.5 and 2.6 are absorbances which result from the stretching modes of CH_3. Typically, symmetric stretching, in which all three C–H bonds extend and contract in sequence, occurs at 2872 cm^{-1}. Asymmetrical stretching, in which two C–H bonds are extending while the third is contracting, typically occurs at 2962 cm^{-1}. These absorbances very closely match the absorbance of bands 2.5 and 2.6.

Calibration Curves

To verify that the reference spectra could be used to reliably determine concentration of HFE-7100, a calibration curve was generated. Spectra for calibrations were performed in the same cell used to create the reference spectra (b = 10 cm). Table 2-4 shows the pressure (P_{HFE}) and corresponding concentration (in molecules/cm^3) of HFE-7100 used to generate the calibration curve.

Data resulting from calibration runs is listed in Table 2-5, with the corresponding plots shown in Figure 2-14. Correlation coefficients confirm what can be seen upon cursory visual inspection of Figure 2-14: bands 1.1 and 1.2 show the most correlation with the theoretical concentrations of HFE-7100. However, it is also interesting to note that the correlation coefficients for the remaining bands are still high, indicating that those bands consistently under-predict the concentrations of HFE-7100.

Table 2-4. Pressures (Torr) and corresponding concentrations (molecules/cm^3) of HFE-7100 used to generate a calibration curve. Gas mixture was 0.05% HFE-7100 in nitrogen.

P_{HFE} (0.05%; Torr)	**Concentration (molecules/cm^3)**
75.5	1.09 x 10^{15}
155.2	2.24 x 10^{15}
301.0	4.34 x 10^{15}
460.6	6.65 x 10^{15}

Table 2-5. Results of RMS analysis calibration curves for HFE-7100 using the eight reference bands. FTIR analysis was performed on a gas sample of HFE-7100 in a cell with a 10 cm pathlength.

Pressure (Torr)	**Concentration (x10^{14} molecules/cm^3)**								
	Band 1.1	**Band 1.2**	**Band 2.1**	**Band 2.2**	**Band 2.3**	**Band 2.4**	**Band 2.5**	**Band 2.6**	**Avg**
75.5	10.7	10.7	5.31	6.60	7.83	6.43	5.54	5.19	7.29
155.2	23.5	23.3	14.9	9.82	31.7	16.9	*	14.8	19.3
301.0	43.0	42.8	25.6	18.5	45.8	26.5	5.12	26.9	29.3
460.6	64.7	63.9	39.1	29.4	68.0	40.7	19.6	37.8	45.4
R^2	0.999	0.999	0.997	0.997	0.979	0.994	0.797	0.994	0.992

**Data unavailable*

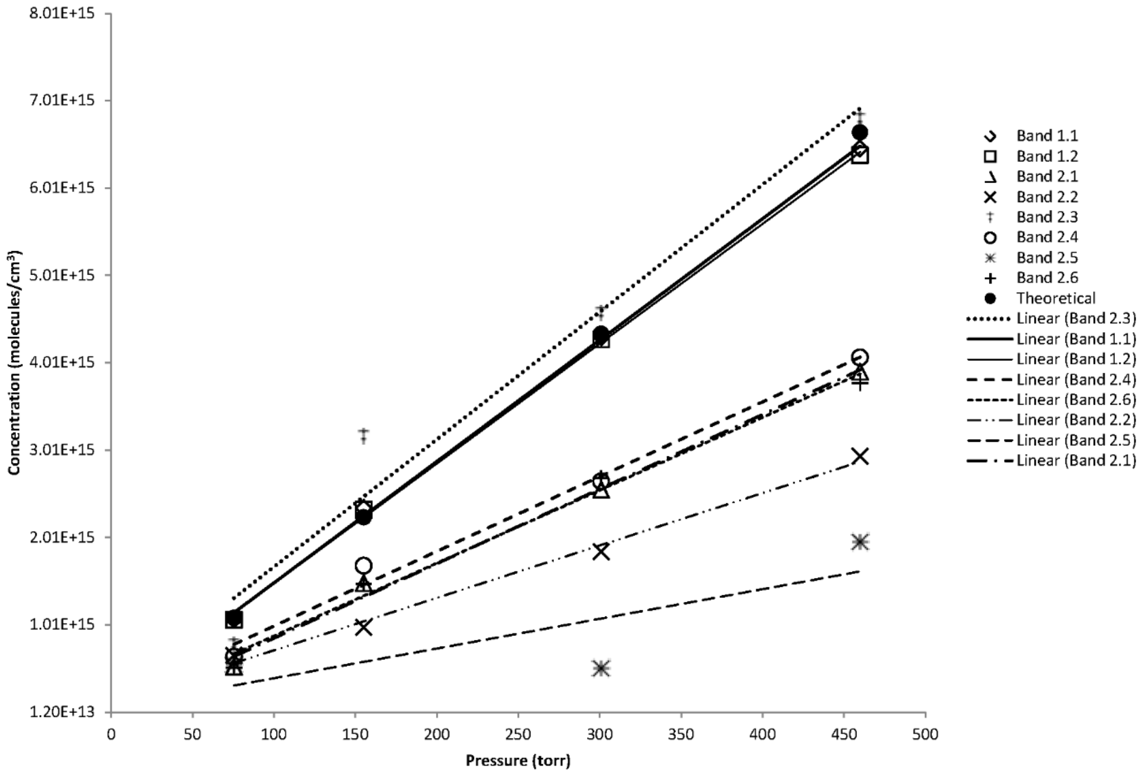


Figure 2-14. Calibration curve of HFE-7100. Concentrations were determined by RMS analysis for the indicated band. FTIR absorbance taken for a gas sample of HFE-7100 in a cell with a 10 cm pathlength.

Figure 2-15 shows the percent difference of RMS-obtained concentrations from the theoretical concentrations. Bands with percent differences closest to zero are more accurate in their determination of concentrations. Based on this figure, it is clear that bands 1.1 and 1.2 provide the most accurate concentrations determinations. With the exception of bands 2.3 and 2.5, which show a high degree of variability, the remaining bands appear consistent in their under-prediction of HFE concentrations.

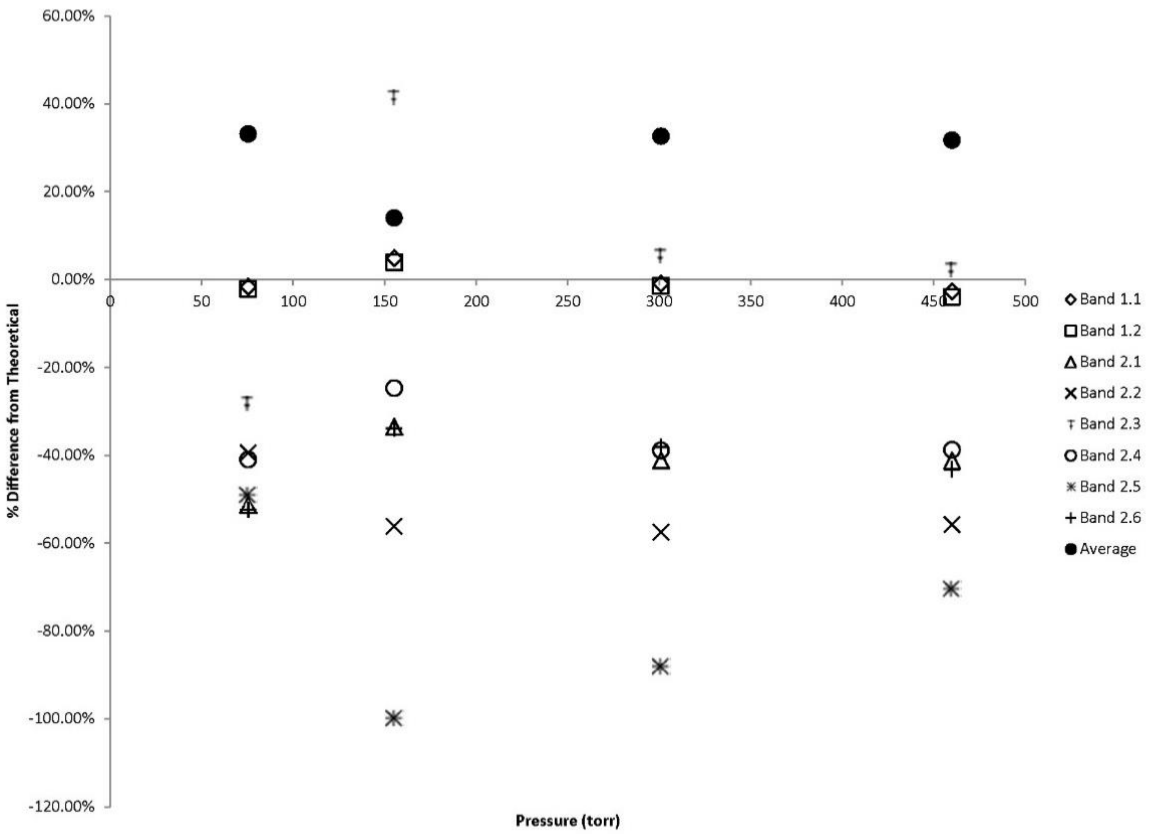


Figure 2-15. Percent difference of RMS-calculated concentrations from theoretical concentrations. FTIR absorbance taken for a gas sample of HFE-7100 in a cell with a 10 cm pathlength.

Identification of Products of HFE-7100 + OH

As shown from the theoretical oxidation pathway above (Figure 2-11), it was expected that COF_2, $CF_3(CF_2)_3OC(O)H$, and CH_2O would be the primary observed products from the OH-initiated oxidation of HFE-7100. Based on the available analysis techniques that were available at the outset of the project (FTIR), this presented a problem. Carbonyl fluoride (COF_2) and $CF_3(CF_2)_3OC(O)H$ would be expected to show strong absorbance bands in the 1000-1400 cm^{-1} region of the IR spectrum due to the vibrations of multiple C–F bonds. This would hinder the identification of products because of the difficulty in separating the spectra of such compounds.

In addition, CH_2O is a weak IR absorber. For these reasons, it was not expected that identification of these reaction products could occur with the sole use of FTIR. To completely identify the reaction products, a mass spectrometer would be necessary. For this reason, a chemical ionization mass spectrometer was coupled to UMBAR through a side port in the flow tube in the detector region. Unfortunately, the mass spectrometer was not functional during the duration of this project.

HFE-7100 + OH Reactions in UMBAR

All chemistry runs were carried out at 50 Torr and 298K. Based on prior work with UMBAR, a standard protocol of flows, described in Table 2-6, was used as a starting point for analysis of the products of HFE-7100 + OH.

Table 2-6. Flows of indicated gases for initial UMBAR reactions of OH + HFE.

Compound	**Flow (sccm)***	**Concentration (x 10^{16} molecules/cm^3)**
Dry air (carrier gas)	5800	-
O_2 (20% of dry air)	-	31
Ar	700	19
NO	20	0.54
H_2	15	0.41
HFE (2.98% in N_2)	20	0.16
N_2†	-	130

**standard cubic centimeters per minute*
†combined from dry air and HFE balance

Abstraction of hydrogen from HFE-7100, the initial step in OH-initiated oxidation, occurs slowly (Figure 2-11). The rate constant of the reaction is k_{OH} = 1.2 x 10^{-14} cm^3 $molecule^{-1}$ s^{-1}.[54] Based on a search of the literature for other possible OH reactions, it appears that there may be an unexpected reaction prior to H-abstraction from the HFE by OH:

Reaction 23 $OH + NO + M \rightarrow HONO + M$
k = 2.8 x 10^{-11} cm^3 $molecules^{-1}$ s^{-1} (*Sander et al.*[57])

Initial HFE + OH runs showed HONO as the only product of the reaction. The RMS results are shown in Figure 2-16. In the figure, products appear below the baseline and reactants consumed during the reaction appear above the baseline. The blue box highlights a poor subtraction of HFE-7100, which is present in both the online and offline scans, likely at a high enough concentration to absorb all light at those wavelengths.

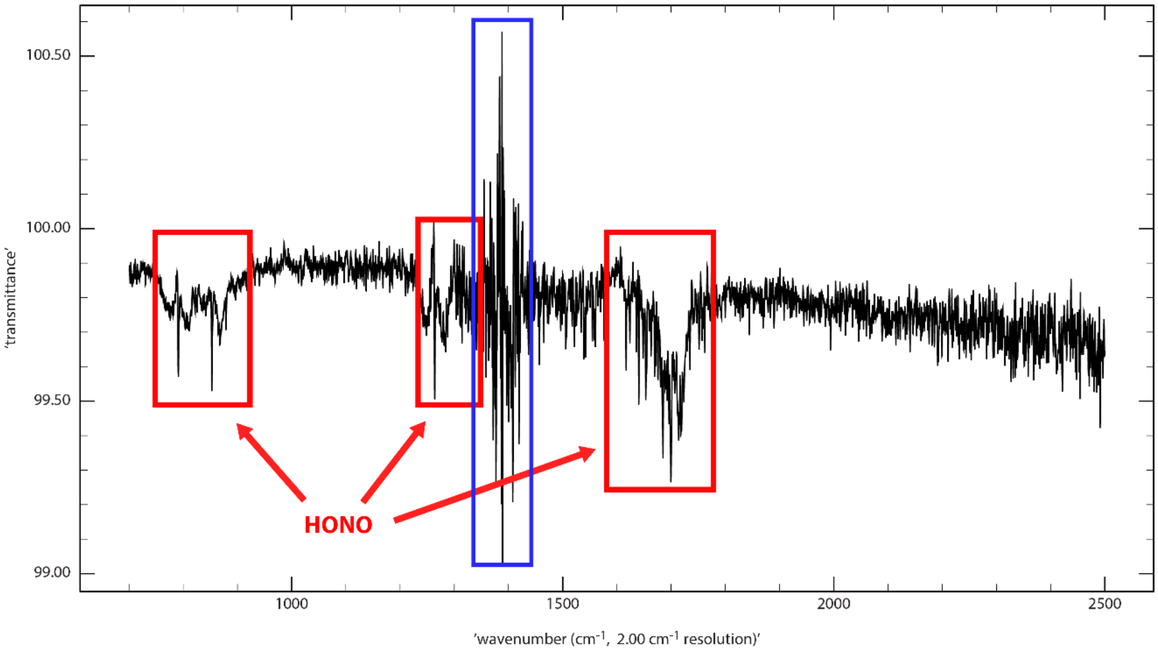


Figure 2-16. RMS results for the presumed reaction of OH + HFE → products. Products appear below the baseline and reactants consumed during the reaction appear above the baseline. Resolution is 2.00 cm^{-1}. The presence of HONO was confirmed by RMS analysis. The blue box highlights a poor subtraction of HFE-7100, which is present in both the online and offline scans, likely at a high enough concentration to absorb all light at those wavelengths.

To verify the occurrence of this reaction, an experiment was carried out in which all the components of the reaction (dry air carrier gas, Ar, NO, H_2, and HFE-7100) were added in sequence, with a new FTIR scan before addition of the next component. Figure 2-17 represents the results of this experiment. Spectrum A is the ratio of the IR spectrum of argon to the IR spectrum of dry air (via a dry air generator). This peak at 2350 cm^{-1} shows that the concentration of CO_2 is increasing as the result of a faulty dry air generator. Spectrum B is the ratio of the IR spectrum of NO to the IR spectrum of argon. This spectrum shows the presence of NO at 1850 cm^{-1} and NO_2 at 1600 cm^{-1}. The presence of NO_2 is a result of the reaction:

(Reaction 24) $2NO + O_2 \rightarrow NO_2$

NO_2 is also produced via Reaction 23 when the radical source is on. Spectrum C is the ratio of the IR spectrum of H_2 (radical source on) to the IR spectrum of the NO addition. This spectrum shows the presence of HONO (~1700 cm^{-1}, Q-branches between 750 and 900 cm^{-1}), verifying the suspicion that OH radicals react with NO to produce HONO, as in Reaction 23. Finally, spectrum D is the ratio of the spectrum of HFE-7100 on to the spectrum with H_2 flowing. Spectrum D shows the presence of HFE-7100, as was expected. All spectra show a noise feature around 1350 cm^{-1} as a result of accumulated nitrates on the KBr windows.

Based on this evidence, along with the known rate constants of the reactions in question (Figure 2-11 and Reaction 23), the reaction of OH + NO occurs more quickly under the conditions of this experiment than the reaction of HFE + OH, indicating that there would be very few observed oxidation products of HFE. To successfully react OH with HFE, it would be necessary to use a source of OH that does not require NO. One such source would be the reaction sequence:

(Reaction 25) $F_2 + \mu w \rightarrow 2F$

(Reaction 26) $F + H_2O \rightarrow HF + OH$

In this scenario, no NO would be necessary for the experimental set-up. HF is a stable reservoir species, and thus would not complicate the chemistry of interest.

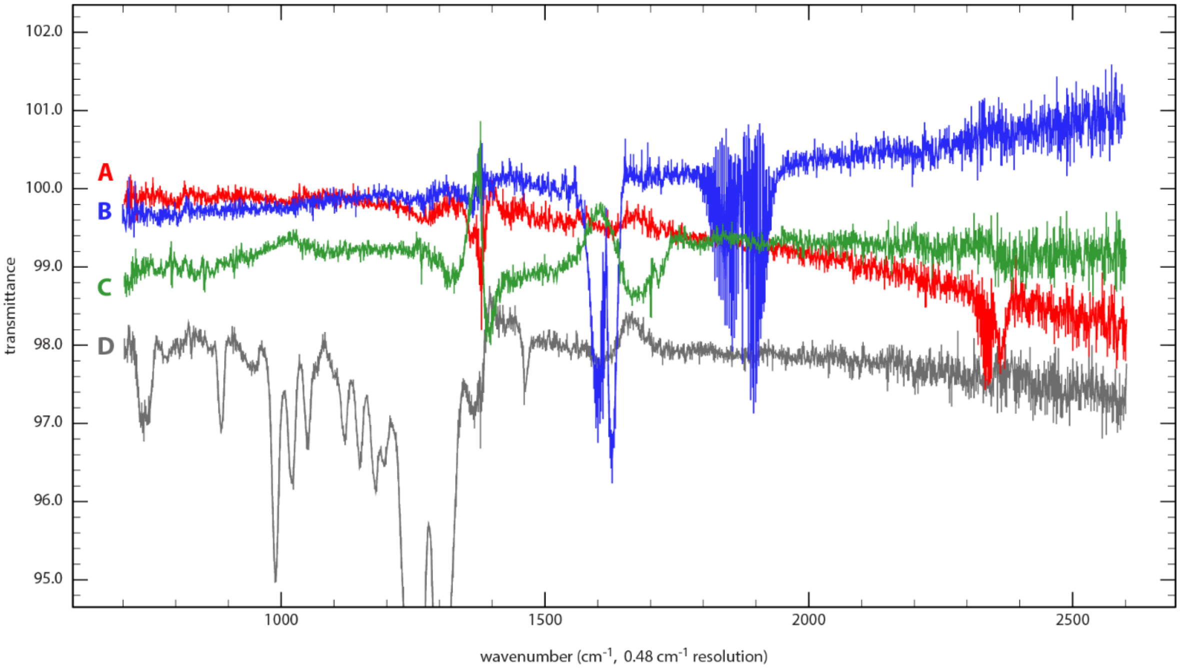


Figure 2-17. Transmittance spectra showing the sequential addition of gaseous chemical species required for reactions in UMBAR. (A) Ratio of argon to dry air. This spectrum shows an increased concentration of CO_2 at 2350 cm^{-1} as the result of a faulty dry air generator. (B) Ratio of NO to argon. This spectrum shows the presence of NO (~1850 cm^{-1}) and NO_2 (~1600 cm^{-1}). (C) Ratio of H_2 to NO. This spectrum shows the presence of HONO (~1700 cm^{-1}, Q-branches between 750 and 900 cm^{-1}), verifying the suspicion that OH radicals react with NO to produce HONO. (D) Ratio of HFE-7100 to H_2. This spectrum shows the presence of HFE-7100, as was expected. All spectra show a noise feature around 1350 cm^{-1} as a result of accumulated nitrates on the KBr windows.

Conclusions

Results of the oxidation of HFE-7100 with OH are inconclusive. During the course of the study, no HFE+OH reactions were observed. In order to determine the first generation OH-initiated oxidation products for HFE-7100, it will be necessary to modify the experimental procedure, including changes to the reagents, reagent flow, and radical source. Additionally, a mass spectrometer will be necessary to identify products containing C–F bonds.

The work presented in this chapter represents an initial contribution to the understanding of atmospheric chemistry and OH-initiated atmospheric oxidation studies. A reference spectrum of HFE-7100 was successfully obtained via a novel continuous flow FTIR method. Calibration results using the reference spectrum showed good fit (up to R^2= 0.999) for most identified bands. It was confirmed that the reaction of OH+NO occurs at a rate faster than OH+HFE. This information is foundational for subsequent work identifying the OH-initiated atmospheric oxidation products of HFE-7100.

Future Work

This work has the potential to be greatly expanded upon. Firstly, it will be necessary to identify appropriate reaction conditions in order to successfully initiate the HFE+OH reaction. Manipulation of the concentrations of HFE, NO, and OH will likely solve this problem. A better solution to the OH+HFE vs. OH+NO reaction kinetics problem is to use an alternative radical source. One such radical source would be to react F with H_2O to produce HF and OH. This source of OH would prove to be better because it does not require NO. The HF produced via this reaction would be unreactive, limiting the chance of unwanted side reactions.

Additionally, HFE oxidation products are likely to contain multiple C–F bonds. These bonds will not undergo any chemistry, thus the IR spectra of the products will show no change from those of the reactants. Because of the nature of the strong IR absorbances resulting from these types of bonds, sampling via mass spectrometry will be necessary for the successful identification of the oxidation products.

Beyond identifying the oxidation products of HFE-7100, there are numerous questions that still require answers. HFEs are a class of compounds, of which HFE-7100 is just one. To get a better picture of the atmospheric and environmental impacts that these compounds can have, more of them need to be studied. Once more of the oxidation products have been studied, we can start to study the products themselves, exploring the potential impacts of these molecules.

Society has an established history of acting on new innovations without fully understanding the repercussions of its actions. If this trend is to change, understanding the full impact of HFEs and their oxidation products is of the utmost importance.

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CHAPTER 3

BENEFITS-COSTS-RISKS ANALYSIS: A CROSS-CUTTING CONCEPT OF THE CHEMICAL THINKING LEARNING PROGRESSION

The need for STEM knowledge extends to all Americans. The products of science, technology, engineering, and mathematics play a substantial and growing role in the lives of all Americans. A democratic society in which large numbers of people are unfamiliar or uncomfortable with scientific and technological advances faces a great economic disadvantage in globalized competition.

-- President's Council of Advisors on Science and Technology[1] --

Introduction and Motivation

In recent years, the reform of science education, both K-12 and postsecondary, has emphasized the need to focus student learning on the development, analysis, discussion, and application of central ideas in the different scientific disciplines.[2,3] Particularly, education policy agencies have highlighted the importance of crosscutting concepts to generate meaningful connections across disciplinary boundaries in science. The National Research Council (NRC) coined the term *crosscutting concepts*,[3] but the notion of core, cross-disciplinary, ideas is not new. The *National Science Education*

Standards referred to them as unifying concepts and practices;[4] the *Benchmarks for Science Literacy* called them common themes;[5] and the College Board used the term unifying concepts in their *Science Standards for College Success*.[6] No matter what they are called, these crosscutting concepts all have the same purpose: to build purposeful bridges that transcend disciplinary boundaries of science and engineering. While these concepts have always been fundamental to a complete understanding of science and engineering, students have typically been expected to build this knowledge on their own[3] in an environment that frequently teaches them isolated facts without contextual explanations.

While crosscutting concepts in educational standards tend to be cross-disciplinary constructs, there can also be crosscutting concepts that are discipline-specific. Sevian and Talanquer[7] have recently identified six crosscutting concepts that can be used to integrate core ideas in the discipline of chemistry. These six concepts include chemical identity, structure-property relationships, chemical causality, chemical mechanism, chemical control, and benefits-costs-risks. Figure 3-1 outlines the six crosscutting disciplinary concepts and the essential questions of chemistry that define each. The work of these authors is aimed at developing a learning progression for *chemical thinking*. Chemical thinking is considered to be:[7]

> *the development and application of chemical knowledge and practices with the main intent of analyzing, synthesizing, and transforming matter for practical purposes.*

The research presented in the this chapter and the one that follows is intended to help develop the learning progressions for two of the crosscutting disciplinary concepts defined by Sevian and Talanquer. Before exploring this research though, it is important for the reader to understand the importance of learning progressions and, more specifically, the aims of the *chemical thinking learning progression*.

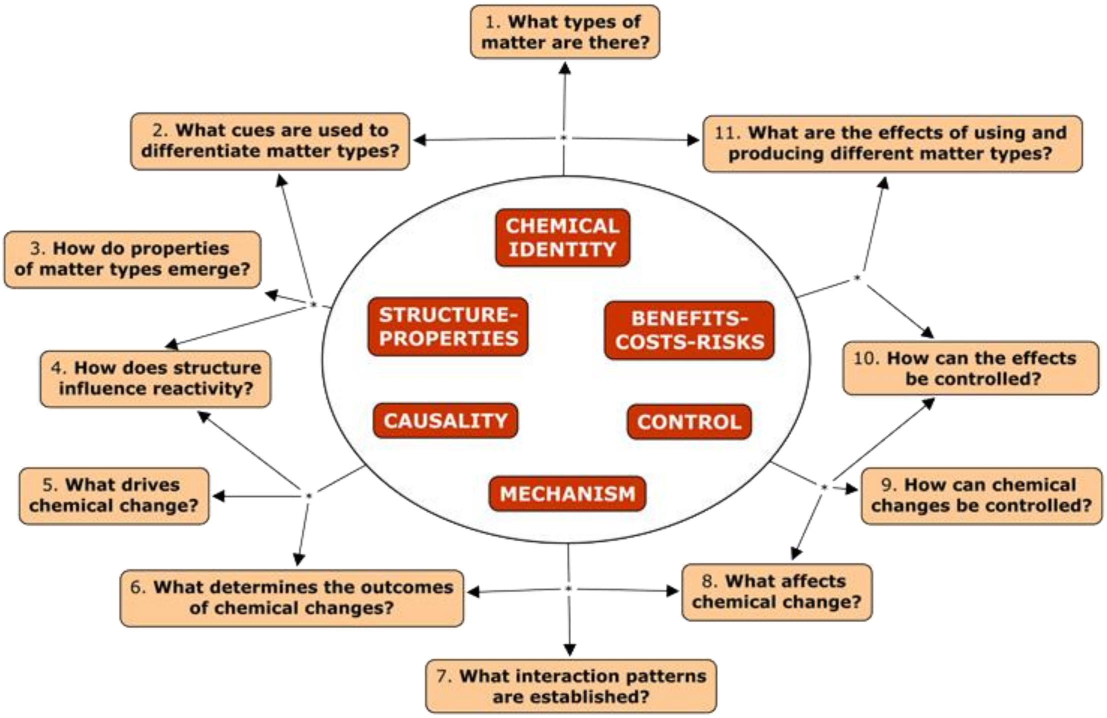


Figure 3-1. The cross-cutting concepts of the *Chemical Thinking Learning Progression.*[7]

Learning Progressions

In recent years there has been a surge of interest in the development of frameworks or approaches to characterize different levels of sophistication and complexity in student knowledge and reasoning in a given domain. This has been the case for research studies in the area of learning progressions (LPs).[8,9] These LPs describe successively more sophisticated ways of thinking about a topic and are based on educational research about how people learn, existing pedagogical content knowledge in the area of interest, as well as on the critical analysis of the structure of the associated disciplinary knowledge.[10]

LPs can be thought of as a picture of the learning landscape exhibited by students. The landscape can be represented by a multi-dimensional map of student understanding similar to a road map – students start at an origin (i.e., their understanding of the world around them) and, hopefully, arrive at the same destination (i.e., mastery of the content), but the path that each individual takes can be different (e.g., different methods of learning, understanding of some concepts more than others). Along their journey across the landscape, students can often get sidetracked by roadside attractions (i.e., cognitive attractors). The map enables tracking of core ideas as individuals progress from novice toward expert in the given area of study. As students become more expert-like in their thinking, it is expected that both the breadth and depth of their knowledge increases.

Learning progressions serve as curriculum models and assessment frameworks, guiding curriculum development as well as instructional and assessment practices to foment more meaningful learning, clearer standards of learning progress, and more useful formative feedback.[11] Development of a successful LP demands a solid understanding of students' ideas and their likely changes with instructional interventions.

Researchers have sought to characterize different aspects of students' understanding in the development of LPs, from understanding of core ideas to ability to engage in science practices.[10] Some of them have paid attention to the evolution of students' mental models of fundamental scientific concepts, such as atomic-molecular structure,[12,13] force and motion,[14] scientific argumentation,[15] the theory of evolution,[16] and genetics.[17] Others have focused on the nature of the explanatory accounts built by students at different levels in a progression[18] or on the quality of students' reasoning characterized in terms of the conceptual sophistication and specificity of the ideas applied, as well as on the validity of the reasoning process.[19] These latter studies emphasize the need to study progress in student understanding based not only on the analysis of the content knowledge that learners demonstrate, but also on how they use such knowledge in particular contexts to build arguments, generate explanations, or make decisions.

Different approaches to characterize distinct levels of sophistication and complexity in student understanding can be identified beyond existing work on LPs. For example, in the SOLO taxonomy defined by Biggs and Collis[20] student responses are allocated to a hierarchy of stages (e.g., prestructural, unistructural, multistructural) depending on the number and level of integration of the elements considered. This taxonomy has been used as a foundational tenet by Claesgens et al.[21] to define and measure performance levels in students' understanding of chemistry, and by Bernholt and Parchmann[22] to assess levels of achievement in science domains. Other scales have been proposed to differentiate how learners use knowledge of different complexity in various contexts[23] or the extent of knowledge integration as determined by the level of accuracy and cohesion of students' explanations.[24]

Based on these types of studies, Sevian and Talanquer[7] have recently suggested a framework for mapping progression in student understanding in chemistry by paying attention to both the conceptual sophistication and the modes of reasoning that students demonstrate when engaged in disciplinary tasks. The authors refer to this framework as the *chemical thinking learning progression*.

Chemical Thinking Learning Progression

The Chemical Thinking Learning Progression (CTLP) is both a theoretical framework characterizing the domain of chemistry as both an investigatory/experimental science and a technoscience in terms of the practice of the discipline, and an analytical framework that provides a means of measuring and accounting for progress in reasoning about and practicing chemistry. As such, the CTLP can be used to interpret the meaning of the practice of chemistry, and to analyze students' reasoning with, and practice of, chemistry.

The CTLP proposes to characterize changes in conceptual sophistication in terms of the evolution of underlying assumptions about the nature of chemical entities and processes that support, but also constrain student reasoning in the domain.[25–27] A focus on "assumptions" facilitates the identification of conceptual resources that may support productive chemical thinking at different educational levels.[28] While part of the aim of the CTLP is to characterize students' modes of reasoning, the focus of the chapters that follow is to describe students' conceptual sophistication in the domain of chemistry.

Benefits-Costs-Risks Judgment and Decision-Making

Chemists, like many professionals, make decisions every day. In the process of decision making, an evaluation of the outcomes is common practice. Unlike many other professions though, chemists' decisions and discoveries have the potential for large-scale impact. For example, the problem of ozone depletion began with the synthesis and identification of the chemical properties of CFCs by chemists in the late 1920s.[29] Unfortunately, those chemists did not the knowledge to consider the risks of widespread use of these compounds. A more complete understanding of the impacts of CFC on stratospheric ozone came in 1974 from Molina and Rowland.[30] These two chemists made claims about the potential risks of CFC usage which spurred an effort to ban the ozone-depleting compounds in the mid- to late-1980s. They won the 1995 Nobel Prize in Chemistry for their work in atmospheric chemistry. The discovery of these two chemists has had global impacts on environmental concerns of the general public, government regulations, and research on refrigerants and propellants.

The work of chemists is also instrumental in identifying problems of global concern. For example, Svante Arrhenius, a Swedish physical chemist, was the first person to link changes in atmospheric carbon dioxide concentration to global climate change.[31,32] Arrhenius' ideas were not fully embraced until the 1970s,[33] but his global-scale thinking is a common theme for chemists.

Given these examples, it is evident that chemists need to be able to perform an evaluation of benefits, costs, and risks (BCR) in the context of their science. However, existing research on students' judgment and decision-making regarding BCR in chemistry is scarce. Science education researchers have studied how students understand chemical processes in the context of modern concerns that involve risks and benefits, including carbon cycling,[18] climate change,[34] hazardous waste management,[35] effects on ecosystems,[36] biotechnology,[37] and nuclear power.[38] Risk psychology researchers have also studied how people consider risk, particularly expert-lay discrepancies, in the context of chemical problems, such as hazardous waste cleanup,[39] health risks with chemical exposure,[40,41] pesticide use,[42] water quality,[43] nanotechnology,[44,45] and nanotechnology as an alternative to carbon dioxide production.[46] Risk perception and cost-benefit analysis are also areas of study within food science and nutrition, with studies that include considering chemical composition in food quality,[47] additives and supplements,[48] and genetic engineering.[49]

Results from the above research studies suggest that people exhibit strong personal preferences or biases in BCR decision making. For example, individuals are known to prefer products and processes considered to be “natural” over those judged to be artificial.[50] Brun found that people classify hazards according to this scheme, and ascribe less risk to natural hazards than to those that are manmade.[51] People tend to perceive “chemicals” as artificial or manmade, and often ascribe a negative connotation to them. In an interview study of over 26,000 European citizens across all 27 European member states, the Eurobarometer project assessed people’s perceptions of chemical products.[52] Respondents generally considered chemicals to be “dangerous or harmful to the environment, rather than useful or innovative” (p. 11). Dickson-Spillmann and coauthors[47] found that people often assume that when chemicals are added to food, the food has greater potential for detrimental health effects. Individuals who have a greater affinity for “natural” food are more likely to hold negative attitudes toward “chemicals.” In general, natural substances and processes are often linked to a subjective impression of goodness, while the products of human intervention are frequently judged more negatively.[50] Such beliefs influence people’s arguments and decisions in many areas of current interest, such as bioethics and gene therapy.[53]

Research in BCR decision making has revealed that laypeople’s judgments are influenced not only by the knowledge or the information they have, but also by the feelings evoked by what they perceive. The positive or negative emotions prompted by words, images, objects, or events affect judgments regarding benefits, costs, and risks, influencing people’s preferences and choices.[54,55] The use of readily available affective impressions to make decisions (affect heuristic) can be easier and more efficient than weighing multiple pros and cons, but may also lead to irrational choices.[56] In the area of risk perception, two primary factors are thought to influence laypeople’s affective impressions: "dread risks" which are characterized by how much a person perceives there to be a lack of control, dread, catastrophic potential, fatal consequences, and the inequitable distribution of risks and benefits; and "unknown risks" which are characterized in terms of a person's assessment of how unobservable, unknown, new, and delayed the risk is in its manifestation of harm.[57] In general, perceived benefit and perceived risk are inversely correlated in people’s minds. In contrast, experts’ perceptions of risk are more closely related to objective evaluations of probability of harm.

Recent studies in the area of argumentation of socio-scientific issues also provide important insights into students' BCR reasoning. For example, research by Kahan et al.[58] suggests that individuals often selectively credit or dismiss evidence of benefits, costs, and risks based on personal values that they share with others rather than on scientific knowledge. In the context of science education, science learners have been found to rely on emotive, intuitive, and rationalistic resources when analyzing socio-scientific issues, independently of their level of content knowledge about a subject.[59,60] Students' ability to generate high-quality BCR analyses seems to vary in a non-linear fashion with content knowledge acquisition.[61] Comparative analysis of decision-making skills between novice students and experts suggests that students' decisions tend to be less integrative and focused more narrowly on particular themes.[62] Novices' decision-making about socio-scientific issues is affected by the use of cognitive heuristics known to bias judgment under conditions of uncertainty, limited time and knowledge, or low motivation to complete a task.[63]

The Role of BCR in Science Education

Standards and policy documents in science education emphasize the need to develop students' abilities to use scientific knowledge and practices to make informed decisions in authentic contexts.[2,4,5] To reach meaningful decisions, individuals must consider a set of factors (social, economic, environmental, ethical) in a process of benefits, costs, and risks analysis. These decision-making practices are becoming especially important for chemists as the specialization of green chemistry emerges as a critical area in their field.

Despite a push from policy-making agencies to develop these skills, the consideration of these factors is barely analyzed or discussed in conventional science classrooms.[64] In the case of chemistry education, dominant curricula at all educational levels focus on the presentation and elaboration of central concepts and ideas in the discipline without much substantive analysis or consideration of the benefits, costs, and risks associated with using chemical products or engaging in chemical practices.[65] Even though chemical knowledge can be expected to play a central role in addressing major problems confronting modern societies, from global warming to food production to availability of alternative energy sources, little class time is spent learning, debating, and reflecting about such topics. Similarly, little research has been done on how students apply their chemistry knowledge in making decisions related to issues that, as those listed above, demand recognizing and weighing a variety of competing factors.

Reform efforts in chemistry education in the past 30 years have led to the development of curricula and instructional practices that more actively engage students in the analysis of authentic problems whose solutions demand the application of BCR analysis and socioscientific decision making.[66] Such is the case of educational projects like *Chemistry in the Community*,[67] *Salters Chemistry*,[68] and *Chemie im Kontext*,[69] at the secondary school level, and *Chemistry in Context*[70] at the college level. Educational research indicates that students' conceptual understanding, attitudes, interests, and motivation for learning chemistry may be heightened by these types of context-based approaches.[71] However, understanding of how learners actually make use of chemistry concepts and ideas, together with other considerations (e.g., environmental, health), in judging costs and benefits and making decisions in more realistic contexts is limited. Although results from research in the field of socioscientific issues shed light on the factors that influence student decision making,[59,72] as well as on the challenges that students face in building arguments to justify their decisions,[73] most of these studies have focused on the general characterization of the type and quality of the arguments built by students when debating highly complex issues involving moral and ethical considerations.

Given the scarcity of research results that can inform the development of instructional models and practices to scaffold student decision making in diverse chemistry-relevant contexts, the central goal of the research presented here was to investigate chemistry students' reasoning when engaged in problems that demanded evaluation of the benefits, costs, and risks of using different chemical products for a specific purpose. In particular, the goal was to characterize, compare, and contrast the types of assumptions and reasoning strategies applied by individuals with different levels of training in the discipline, from undergraduate students to graduate students to practicing chemists. The project was motivated by the belief that, in order to align chemistry education with current visions for science education in the US[2,3] and other countries,[74,75] it is necessary to enrich the understanding of how knowledge of core ideas and practices progresses with training in the domain of chemistry.[8] Results focus on characterizing different levels of sophistication in the analysis of problems that demand application of chemistry concepts and ideas, together with careful judgment and consideration of potential environmental, safety, and health benefits, costs, and risks of chemical products and activities. A characterization of this type was developed using a framework of learning progressions as part of a larger project on chemical thinking.[7] The findings have implications not only for the preparation of green chemists and engineers, but also of scientifically literate citizens who should be able to judge the broader implications of their decisions.

Refrigerants Case Instrument

In order to study BCR analysis in participants, a case study was used in a pilot implementation. Cases provide practical scenarios in a real-world context that can be used to introduce new content in the process of learning. Cases are often used in problem-based learning and case-based learning pedagogies.[76–79] A cursory review of relevant literature on the development of case studies[80–82] provided insight on how to compose a relevant and useful case. Because of the author's prior knowledge and experience researching refrigerants, the case was designed around that topic. Additionally, several of Herreid's principles[81] were used as guideposts, namely that a good case should: tell a story, be conflict provoking, force the reader to make a decision, include quotations, create empathy with the central characters, and be short. The case was written so that each possible outcome had both positive benefits and negative costs or risks in order to explore participants' abilities to draw on their BCR analysis skills.

Methodology

Setting and Participants. Participants were recruited from two universities in different regions of the United States. First-year general chemistry students (n=9) were recruited from a medium-sized non-traditional public university in the northeastern United States (Univ 1) during the summer semester of 2012. From this same university, graduate students (n=4) and professors (n=2) in the chemistry department also volunteered for the study. Also during the Summer 2012 semester, students taking organic chemistry (n=26) were recruited from a traditional medium-sized public university in the southeastern United States (Univ 2). Instructors of these courses offered extra credit to students who were willing to participate in the study. Sample sizes were intentionally kept small in order to facilitate the qualitative analysis of the pilot study data. Individual consent to participate in the study was obtained following procedures approved by the Institutional Review Board at the primary institution. Table 3-1 shows the demographic distribution of the participants.

Table 3-1. Demographic distribution of study participants.

	Gender		**Total**	**Course enrolled in when interviewed**
	M	**F**		
Univ 1 (GC)	4	5	9	General Chemistry I
Univ 2 (OC)	12	14	26	Organic Chemistry I
Experts (EXP)	4	2	6	-
Total	**17**	**22**	**41**	

Data Collection. Participants were asked to read a two-page case study, answer a six-question survey, and participate in a follow-up interview about their responses. The refrigerant case study (RCS) presented the participants with a scenario in which they were a member of an executive board for a company that manufactures air-conditioning units. In the scenario, the board has to vote on which chemical refrigerant the company will use in a new line of air-conditioning units that it will manufacture. At the board meeting, three unique compounds are presented as refrigerant options: sulfur dioxide (SO_2), a hydrochlorofluorocarbon (HCFC), and a hydrofluorinated ether (HFE). Three chemists in attendance at the meeting each argue for one compound and against the other two. Their arguments provide information in three areas of consequence: economic, environmental, and human health. For example, one chemist argues that SO_2 is the cheapest to produce among the three choices and that the HFE could cause environmental hazards because its atmospheric degradation products are unknown. All of the chemists' arguments are summarized in Table 3-2. The case study is reproduced in its entirety in the Appendix.

Table 3-2. Summary of arguments presented in the Refrigerants Case Study.

	CONSEQUENCES		
COMPOUND	**Economic**	**Environmental**	**Health**
Sulfur Dioxide (SO_2)	• Least expensive	• Primary component of smog • Causes acid rain	• Inhalation causes sickness or death.
Hydrochlorofluorocarbon (HCFC)	• Mid-range cost	• Highest ODP and GWP	• Mild irritant
Hydrofluorinated ether (HFE)	• Most expensive	• Atmospheric byproducts unknown	• Mild irritant

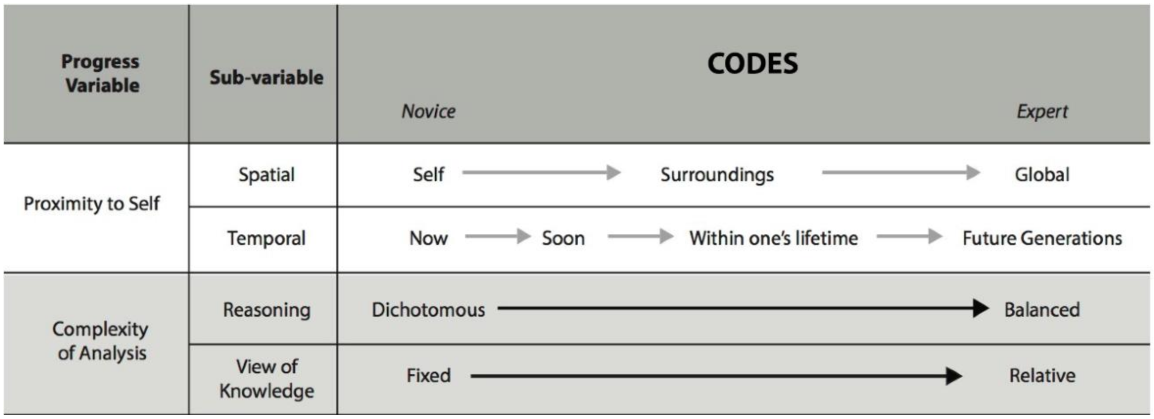
After reading the case study, participants were given a six-question open-ended survey to complete. The purpose of this investigation was to understand the reasoning and motivations for the decision that the participants made. To this end, the questions were structured in such a way as to ascertain the underlying thinking and overall reasoning of the participant during the decision-making process.

Because this was an exploratory study, follow-up interviews were conducted with participants to verify that a complete understanding of the participants' thinking was captured. Follow-up interviews were semi-structured, using the questions presented in the written survey as a guide, and lasted an average of 15 minutes. Interviews were audio-recorded and later transcribed for coding. Analysis of the written surveys and interview transcripts indicated that the surveys alone were not robust enough to capture the data sought. For this reason, the results presented here are based mostly on an analysis of the interview transcripts.

Data Analysis. An iterative, non-linear constant comparison method of coding was applied,[83] using web-based qualitative analysis software (Dedoose) to facilitate the analytical process. Interview transcripts were first analyzed and coded to identify the features noticed and used by different participants in making their decisions. Common codes were grouped together into themes for further analysis. Existing literature on the psychology of risk and decision-making aligned with the discovery of some common themes that were identified throughout the interview transcripts. Raters used an iterative process to reach consensus on a coding structure and, ultimately, the identification of two key themes. Examination of trends that occurred when comparing educational levels led to the association of these themes as progress variables. Progress variables have been described as dimensions of student knowledge along which progress is expected to occur.[7,11]

Results and Discussion

Two primary progress variables (Figure 3-2) were uncovered: PROXIMITY TO SELF and COMPLEXITY OF ANALYSIS. PROXIMITY TO SELF reasoning occurred when participants reasoned about the distance to which the risk would occur to them. Within the PROXIMITY TO SELF variable, participants showed reasoning about both SPATIAL proximity and TEMPORAL proximity. All participants used spatial proximity in their reasoning, often at more than one level, but only 73% of participants (n=30) had explanations that used temporal proximity. COMPLEXITY OF ANALYSIS describes the traits of participants' analyses based on the type of reasoning they used and the way in which they viewed knowledge. Because there was a clear indication of two traits in their reasoning, participants were assigned, at minimum, two codes within the COMPLEXITY OF ANALYSIS variable, one code from the REASONING sub-variable and one code from the VIEW OF KNOWLEDGE sub-variable.



Progress Variable	Sub-variable	CODES (Novice → Expert)
Proximity to Self	Spatial	Self → Surroundings → Global
	Temporal	Now → Soon → Within one's lifetime → Future Generations
Complexity of Analysis	Reasoning	Dichotomous → Balanced
	View of Knowledge	Fixed → Relative

Figure 3-2. Summary of progress variables and coding structure of Refrigerant Case Instrument interviews. Codes are arranged left-to-right in order of increasing sophistication.

Each participant response contained at least one explanation. These explanations were coded with two COMPLEXITY OF ANALYSIS codes and at least one PROXIMITY TO SELF code. A minimum of three and a maximum of eight codes were assigned to participant responses. On average, five codes were assigned to each participant response.

Proximity to Self. Participants frequently reasoned about the risks associated with the choice of compound based on the proximity (i.e. closeness) of the risk to themselves. This reasoning occurred along both a temporal thread (i.e. how soon the effect of the risk would become relevant) and a spatial thread (i.e. how close the effect of the risk would occur to them). Individuals who demonstrated reasoning at a novice level of thinking appeared to be constrained by reasoning about the risks at proximities closest to themselves, labeled SPATIAL-SELF, SPATIAL-SURROUNDINGS, TEMPORAL-NOW or TEMPORAL-SOON. This constraint manifested in individuals having concern for only those risks that would have the greatest effect on humans (i.e., SELF) or the environment (i.e., SURROUNDINGS), either immediately (i.e., NOW) or in the very near future (i.e., SOON). For example, one general chemistry student said:

> **GC7:** *SO_2 is too toxic for us to use and the risk of human sickness or death is not worth the cheapness. For all I know, we could be in court paying a settlement that is more money than what we would have paid out to use a more expensive chemical.*

Throughout her interview and written responses, this student indicated that the primary basis of her risk reasoning dealt with effects that would occur NOW and to SELF. However, this became less clear at later points in her interview. While she stated that environmental and long-term effects were of a concern, she never clearly indicated them in her reasoning. For example, when she explained what she meant by "safety" she said:

> **GC7:** *When I looked at SO_2 and then the HFE…um, I was just like there's unlimited things that could go wrong by picking those, and even though I didn't know too much about HCFC, I was just like it doesn't have as many negatives as those two, so I was just like that's why I'll pick it. So I picked it. And I mean, I also put in there that I wasn't given as much information. I wanted to see like poster boards or something about "Well this is what would happen over 20 years." Or "This is what could happen short term. Long term."*

Participants like GC7, who exhibit novice reasoning, showed no evidence of reasoning about distal proximities, even if they did state that these scales were of a concern. In fact, 57% (n=20) of the participants who had codes for SELF or SURROUNDINGS and 22% (n=5) of those who had codes for NOW did not appear to show reasoning at more distal proximities for this case. This is illustrated by an organic chemistry student when she chose to base her decision entirely on human health consequences, but explained how it would also have secondary economic consequences:

> **OC5:** *The HFE was the best, although the cost was really high. You cannot have customers if you harm the customers: no customers, no money. If the company can create a loyal customer base, then the money will continue to pour and so on and this would counter the high cost of HFE.*

OC5 also thought effects on the surroundings were important, but failed to explain how or why they related to her decision.

> **OC5:** *By purely going off of what they said, I obviously don't want to harm the customers. Sulfur dioxide should be taken off the list. Between the other two, the cost difference and effect on the environment are very important. I'm assuming that there isn't that much difference between the cost.*

OC5's explanation is typical of participants who lacked a higher level of content knowledge about chemistry and were thus unable to integrate such knowledge in their reasoning. This was evidenced later in this same interview when OC5 indicated that environmental factors should be considered, but despite prompting by the interviewer, she did not elaborate on which environmental factors were relevant to consider or how the information in the case was related to any environmental factors. In the conclusion of her decision, although she had said that environmental factors were important to consider, she elevated immediate human health risks above environmental factors.

It was in the PROXIMITY TO SELF progress variable where participants used their knowledge of chemistry to inform their decisions. The level of sophistication of the participants' chemistry knowledge allowed for the identification of the novice to expert progression. Reasoning based on the distant proximities, using implicit assumptions of SPATIAL-GLOBAL, TEMPORAL-WITHIN LIFETIME, or TEMPORAL-FUTURE GENERATIONS, was evident in graduate students and faculty (66%, n=4), organic chemistry students (54%, n=14), and general chemistry students (22%, n=2). For example, a graduate student was asked during her interview what information she thought was relevant:

> **EXP3:** *I thought the chemical structure was relevant because then you could see visually…I could picture how it would degrade in the atmosphere and also you can tell from the structure whether or not it will absorb IR radiation. I could tell if it was a greenhouse gas. And then the environmental effects, like acid rain, smog, ozone depletion and global warming potential [were also relevant].*

EXP3 clearly brings a more sophisticated level of chemical knowledge to bear on the problem. Her use of that chemical knowledge, though, is primarily applied to her reasoning about how these compounds will have global implications (e.g. global warming via IR absorption).

Participants who used more expert chemistry knowledge showed an ability to understand the risks associated with distant proximities as well as closer proximities, but typically made their final decisions based on the bigger picture. All participants who reasoned at a GLOBAL proximity (n=16) also reasoned at the proximities of SELF and SURROUNDINGS. For example, one expert, a professor, demonstrated reasoning at both proximate and distal proximities in his interview:

> **Interviewer:** *Do you think there is enough information in what the scientists are presenting to make an informed decision?*
>
> **EXP5:** *Well you start by throwing out* SO_2*. It's not as effective of a refrigerant for one thing, but the other thing is that it's been used as a refrigerant and it had bad consequences and it's very toxic.* SO_2 *leaks are disastrous from the immediate toxicity problems but also it's bad once you get them into the atmosphere...as a greenhouse gas…as a variety of things. So* SO_2 *is just a horrible choice, and so you start making the decision by throwing out one of them and then you talk about the ones that have some unknowns.*

EXP5's decision is based on some prior knowledge that informs him about the multiple dangers of sulfur dioxide at both the proximities of SELF and GLOBAL.

A summary of the coding of participants' ideas in the PROXIMITY TO SELF progress variable, sorted by level of education, is shown in Figure 3-3. As shown in the graph, it appears that general chemistry and organic chemistry students primarily reason at the novice level (i.e. self, surroundings, now, and soon). This may be because participants at lower education levels have not yet acquired sufficient chemistry knowledge necessary to reason at more distal proximities. This claim is supported by the clear usage of both proximal and distal proximities by experts.

It is also evident from Figure 3-3 that temporal proximity is considered infrequently in the decision-making process. It is interesting to note that responses from experts did not consider the “Soon” proximity. Instead, they appear to lump together all near-term effects into “Now”.

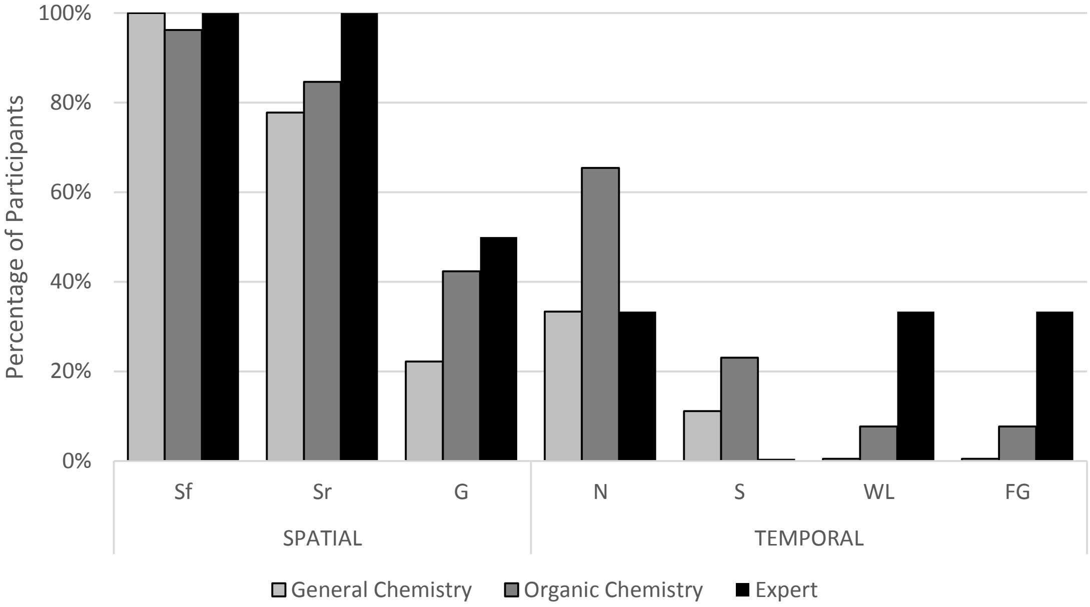


Figure 3-3. Percentage of participants within each education level who were identified as having at least one occurrence of the indicated proximity in the *P*ROXIMITY TO *S*ELF progress variable. Some participants reasoned at more than one proximity within the SPATIAL or TEMPORAL sub-variables, so the percentages do not add up to 100%. [*Sf: self; Sr: surroundings; G: global; N: now; S: soon; WL: within lifetime; FG: future generations*]

Complexity of Analysis. A second progress variable along which participants’ evolution of assumptions was observed was the complexity with which risks were analyzed. The COMPLEXITY OF ANALYSIS in participants’ responses related to two common themes: REASONING and VIEW OF KNOWLEDGE.

The first theme that appeared to influence participants' analysis is the variety of information incorporated into their reasoning (i.e., the REASONING sub-variable). Participants demonstrating a lower level of sophistication along the REASONING progress variable tended to focus on a single factor, neglecting all other information that was provided in the case study or that they may have brought to bear from their own prior learning or experiences. In this study, reasoning of this type was labeled DICHOTOMOUS. Dichotomous reasoning was seen in 44% (n=18) of participants. The following excerpt, taken from the interview of a general chemistry student, provides a good example of dichotomous reasoning when considering refrigerants as either toxic or benign (i.e., two extremes):

> **GC6:** *HFE is the best choice due to its stability and non-toxic effect on the environment and those around it. Both [the] HCFC and SO_2 are clearly drawbacks to the direction that this company is heading towards and are both harmful to the environment and our customers. HFE is a benign product that I stand behind for the refrigerant.*

GC6 reduces each compound to a single variable – either "good" or "bad" – and makes his decision solely this newly synthesized variable. The HFE is "good" because of its stability and limited toxicity, whereas the HCFC and SO_2 are simply "bad". This way of reasoning demonstrates a dichotomous scenario that GC6 is using to simplify his decision.

An organic chemistry student also demonstrated dichotomous reasoning in his analysis of the decision:

> **OC23:** *I thought the hydrofluorinated ether will be the best compound because it was the most stable and it is non-toxic. If someone inhaled it, it is only a mild irritant. If they find something wrong with it, they can just change it just like they did for the CFCs.*

OC23 bases his decision solely on the HFE’s properties even though there are many other factors that could be considered when making a decision.

This type of reasoning has also been observed among novices by other researchers.[84,85] In the literature, it has been called a one-reason decision-making heuristic, and is characterized by a person using a single piece of information, frequently stopping the search at the first feature noticed that can be used to make a choice.[86] Todd and Gigerenzer, who have studied fast and frugal heuristics to great extent, explain this heuristic as a way of conserving mental effort under conditions of limited time: “combining information from different cues requires converting them into common currency, a conversion that may be expensive if not actually impossible”.[86] In chemistry, the one-reason decision-making heuristic has been observed among novices when predicting solubility,[87] making judgments about chemical reactivity,[88] determining molecular polarity,[89] and making predictions about changes in thermodynamic properties.[90]

At the more sophisticated end of the reasoning spectrum, participants explained their reasoning with multiple, sometimes unrelated pieces of information. This more complex approach to arguing was considered in this study as BALANCED reasoning. An undergraduate student enrolled in general chemistry, demonstrated balanced reasoning when she presented a more complex argument with multiple points of reasoning:

> **GC9:** *I chose HCFC mostly because there have been a lot of studies and there is a lot of information. There are some impacts on the environment, but it has no impact on human health. It is a little more costly than SO2, but it is worth it especially if you are dealing with lawsuits if someone becomes sick or harmed by it. For the HFE, there is no information about it.*

Her response seems to indicate that she is thinking about the problem in a multi-faceted, or balanced, way – pulling information from multiple aspects of the problem. Instances of BALANCED reasoning were identified in 63% (n=26) of participants.

Studies of expert decision making are scarce in the literature. From the fields of economics, mathematics, and philosophy, *decision theory* provides a means for logical analysis in making decisions among alternatives.[91,92] Decision theory provides an accounting of the logic for each of the possible decision paths. Two main branches of decision theory exist: (1) decision under uncertainty in which alternative courses of action have outcomes with unknown probabilities of occurrence, and (2) decision under risk in which the probabilities of occurrence of particular outcomes is known. Decision-making in environmental systems typically exists as decision under uncertainty. Within this branch, three decision paths exist, depending on what is compared. A *maximin* decision maker pursues a decision in which the detriment of the outcome is minimized. Such an individual, therefore, could be considered a pessimist, arguing based on acceptance of a worst-case scenario and making a decision where the consequences are minimized. A *maximax* decision maker pursues a decision in which the benefit of the outcome is maximized. Such an individual could be considered an optimist, determining the benefits of each outcome and making a decision in which the benefit is maximized. A *minimax regret* decision path, also known as an opportunity loss path, compares differences between the actual outcome and the better position that could have been attained if a different course of action had been chosen, and argues for choosing the option with the least difference. While many participants' reasoning could be mapped to one of these decision paths, BALANCED reasoning provided a fuller explanation that incorporated more relevant information.

The second theme related to COMPLEXITY OF ANALYSIS is how participants treated the information in their responses (i.e., the VIEW OF KNOWLEDGE sub-variable). At the lower level of sophistication, participants demonstrated a view that scientific knowledge is immutable. This type of knowledge view was coded as FIXED. Participant GC6 (see excerpt above) demonstrated a FIXED view of knowledge. His entire argument is based on the statement that HFE is benign, but he discounts what the scientists said about there being very little information on the full environmental effects of the HFE. A fixed view of knowledge was seen in 58% (n=28) of participants.

On the other hand, some participants demonstrated an understanding that scientific knowledge is always growing and changing. OC23 was one such participant (see excerpt above). His statement “if they find something wrong with it” implies that he knows that it is possible for more information to be uncovered, thus the current state of knowledge on the subject (i.e., his VIEW OF KNOWLEDGE) is not fixed. This view of knowledge was referred to as RELATIVE and was seen in 41% (n=17) of participants. It is important to note that of the participants exhibiting a fixed view of knowledge (n=28), 14% of those (n=4) also demonstrated a relative view of knowledge later in their interview.

The notion of differing "Views of Knowledge" is not a new finding. Literature on the nature of science (NOS) highlights the common, and mistaken, belief that scientific knowledge is absolute or certain.[93–95] Several instruments have been used to understand students' views of NOS including the Science Attitude Questionnaire[96] and the Test on Understanding Science.[97–101] In all of these instances, the view that scientific knowledge is not tentative was predominant. Although the use of these instruments has been declining, there are recent studies that illustrate consistency across the decades.[102–104] Findings from this study are in line with these results, with students in both general and organic chemistry demonstrating a primarily fixed (i.e., absolute or certain) view of knowledge. Scientists' views on NOS have also been studied. Particularly interesting is that Behnke[105] sampled 300 scientists using a 50-statement questionnaire in order to gauge their understandings of NOS. It was found that 20 percent of these scientists felt that scientific findings were not tentative. Results of this study show no experts that hold a relative view of knowledge.

Figure 3-4 shows the percentage of participants at each education level who demonstrated at least one occurrence of the indicated code. There are some cases where participants reasoned at multiple levels within each sub-variable, so it is possible that some groups do not sum to 100%. The general chemistry group, which primarily displayed novice levels in the PROXIMITY TO SELF progress variable (Figure 3-3), does not show the same trend in the COMPLEXITY OF ANALYSIS progress variable. This is indicative of a clear separation of participants' ability to use chemistry knowledge (PROXIMITY TO SELF) from their ability to reason through a decision (COMPLEXITY OF ANALYSIS), which is discussed further in the following sub-section.

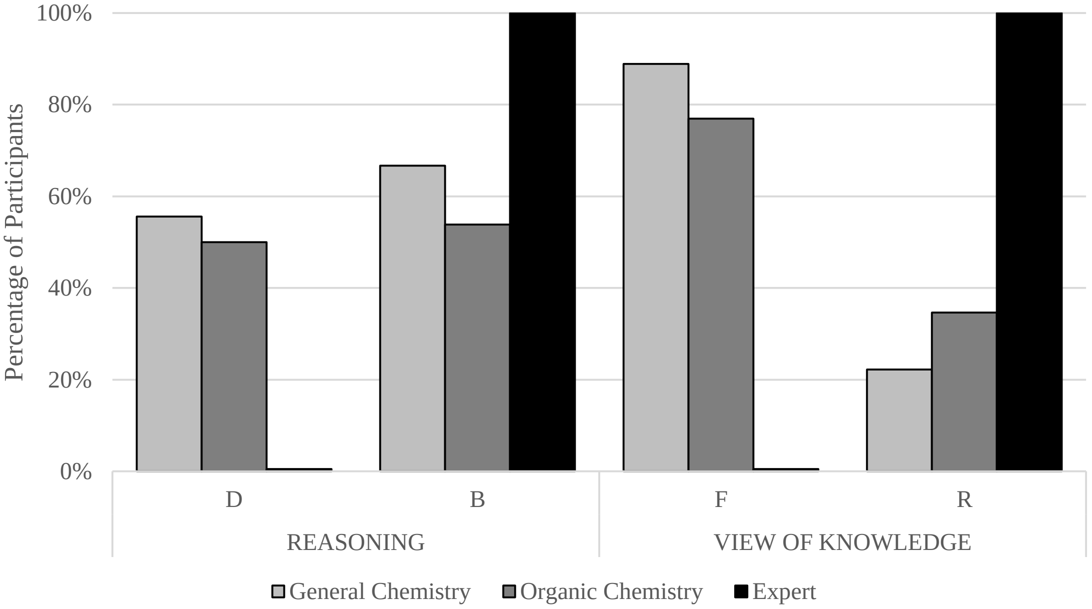


Figure 3-4. Percentage of participants within each education level that who identified as having at least one occurrence of the indicated code in the COMPLEXITY OF ANALYSIS progress variable. [*D: dichotomous; B: balanced; F: fixed; R: relative*]

Relationships Among Progress Variables. The COMPLEXITY OF ANALYSIS and PROXIMITY TO SELF progress variables are distinguishable by both the content of the reasoning and the level of conceptual chemistry knowledge displayed. Both appear to play an important role in a person's ability to analyze the benefits, costs, and risks of a given situation. Therefore, it is possible for a person to be at the expert level in

COMPLEXITY OF ANALYSIS but at the novice level in the PROXIMITY TO SELF variable. The inverse is also possible, with a novice level of COMPLEXITY OF ANALYSIS but an expert level along the PROXIMITY TO SELF sub-variable.

Table 3-3 shows the percentage of participants with specific implicit assumptions co-occurring in their interview. Some individuals demonstrated novice level thinking at the beginning of their interview, but eventually displayed more expert thinking before the end of their interview. Thus, there are some instances where participants' reasoning was characterized by more than one code within the same sub-variable.

Further attention was paid to specific trends that were observed in the data. First, participants who reasoned with a GLOBAL view of PROXIMITY TO SELF (39%) also showed reasoning with the views of self (39%) or surroundings (37%). This provides evidence that more expert individuals show an ability to reason at multiple levels. Secondly, the percentage of participants who demonstrated both a fixed view-of-knowledge and balanced reasoning (41%) is higher than the percentage of participants who showed a relative VIEW OF KNOWLEDGE and balanced REASONING (32%). This indicates that the level of reasoning ability an individual displays does not necessarily correlate to the way he or she views knowledge. While this appears to be an important relationship, there is not enough evidence from this pilot study to explore further.

Table 3-3. Implicit assumption co-occurrence table showing percentage of participants (N=41) with the top and left codes occurring within their interview. *D: dichotomous; B: balanced; F: fixed; R: relative; Sf: self; Sr: surroundings; G: global; N: now; S: soon; WL: within lifetime; FG: future generations.*

	COMPLEXITY OF ANALYSIS[a]				**PROXIMITY TO SELF[a]**						
	Reasoning		**View of Knowledge**		**Spatial**			**Temporal**			
	D[b]	B	F[b]	R	Sf[b]	Sr[b]	G	N[b]	S[b]	WL	FG
D[b]		7	34	15	41	37	15	20	15	2	2
B			41	32	63	56	29	39	2	5	7
F[b]				10	68	56	24	41	12	2	5
R					39	39	20	20	5	5	5
Sf[b]						83	39	51	17	5	10
Sr[b]							37	44	15	7	10
G								27	10	5	5
N[b]									5	7	2
S[b]										2	0
WL											0
FG											

[a] *Percentage of co-occurrence of implicit assumptions*
[b] *Indicates novice level. All others considered expert level.*

Summary

This pilot study, developed as an initial exploration of the BCR analysis thinking of chemistry novices and experts, provided valuable information to develop further instruments for investigation of this topic. The results replicate some results seen by other researchers, and indicate that an ability to reason at various spatial and temporal proximities is closely tied to conceptual understanding in the domain. The data also show that the complexity with which individuals evaluated the provided scenario did not necessarily correlate to their ability to reason at more or less expert proximities; thus analysis of a problem does not correlate with level of knowledge in chemistry.

While the Refrigerant Case instrument provided a good foundation for some initial findings on BCR thinking among student and expert participants, a limitation was experienced with the study's design: the problem that serves as the scenario is based on chemistry content that is at too high a level for some first year undergraduate chemistry students. This made it difficult to fully explore certain aspects of the BCR construct (i.e., how students use chemistry knowledge to reason about BCR). Since a majority of participants lacked a deeper knowledge and understanding of most chemical concepts relevant to the case, it was only possible to uncover general reasoning within the two main variables using this this instrument. The second instrument, discussed in the following sub-sections, was designed to more thoroughly investigate BCR at a content level more suitable to participants from a wide range of educational levels.

In the subsequently developed instrument the PROXIMITY TO SELF progress variable evolved to represent participants' conceptual sophistication (i.e., how they use chemistry knowledge) and the COMPLEXITY OF ANALYSIS progress variable evolved to represent participants' modes of reasoning (i.e., the complexity with which they structure their response).

GoKart Evaluation-Based Instrument

The second phase of this work focused on the analysis of the knowledge, assumptions, and modes of reasoning expressed by individuals with different levels of training in chemistry when engaged in a task that demanded the evaluation of the benefits, costs, and risks of using different chemical substances. Particular interest was paid to identifying and characterizing different levels of sophistication in BCR reasoning in chemistry contexts. The first instrument, discussed above, was developed to explore the general nature of benefits-costs-risks thinking using chemistry knowledge. The Refrigerant Case instrument indicated two progress variables along which the development of chemical thinking can be characterized: PROXIMITY TO SELF and COMPLEXITY OF ANALSIS. These variables corresponded well to the chemistry-specific and domain-general progress variables of the chemical thinking learning progression (CTLP). Therefore, a second instrument, hereafter referred to as the GoKart Instrument, was designed to be able to use the CTLP as an analysis framework to uncover students' assumptions. Because BCR thinking encompasses consideration of consequences, of the three pedagogies defined by the CTLP, the evaluation pedagogy was selected as the most appropriate pedagogy for this instrument. Evaluation pedagogies are concerned with "considering, weighing, and judging the social, economic, and environmental benefits, costs, and risks of chemical products and activities".[7]

Methodology

Setting and Participants. Participants were recruited from chemistry courses taught at the University of Massachusetts Boston (UMB). In accordance with UMB's IRB approval, student participants were volunteers contacted via their research advisors or in class, with the instructor's consent, and were offered small denomination gift cards or course extra credit. Table 3-4 shows the distribution of participants by chemistry education level. Racial ethnicity of participants was a typical sampling of the university's population: 46% Caucasian, 7% African American, 11% Asian, and 36% from other ethnicities. For reference and privacy purposes, a label was assigned to each individual based on their level of training in the discipline (freshman, F; sophomore/junior, SJ; senior, S; graduate, G; professor, P) and their position on an interview list. For example, the second freshman on this list was assigned the label F2.

Table 3-4. Distribution of participants by chemistry education level.

Chemistry Education Level (Abbr)	N	Course Enrolled In
Freshman (F)	11	General Chemistry
Sophomore or Junior (SJ)	11	Organic or Analytical
Senior (S)	7	Final year of studies
Graduate Student (G)	5	--
Professor (P)	5	--

Data Collection. Participants were presented with a scenario in which they were asked to design a GoKart for an amusement park. As part of their design process, they had to select from one of four available fuels to power the GoKart. A semi-structured interview protocol was used. The interview protocol was designed to first freely explore factors that influenced participants' judgments and decisions, and then test the extent to which interviewees considered physical and chemical properties such as state of matter, chemical composition, and molecular structure as relevant cues in making their choices (main questions summarized in Table 3-5; full interview protocol reproduced in the Appendix). A key feature of the instrument's design is that there is no one right answer to the choice of fuel. The decision made by the participant depends entirely on what cues he or she feels are relevant to make a decision. Even experts do not agree on an answer.

Thus, the objective was not to investigate whether students could arrive at the correct answer, but to explore their reasoning strategies.[88] While the interview protocol was used to probe student reasoning about multiple areas of the chemical thinking framework,[7] only the fifth question was designed to evaluate BCR reasoning strategies and content usage.

Table 3-5. Semi-structured interview protocol for the design-based problem interview. The column on the left lists the questions asked. The column on the right lists the intent of the corresponding questions. Follow-up questions aimed at uncovering the items listed in the question's intent. Reproduced from Sevian and Talanquer.[7]

Scenario: An amusement park has asked you to design a GoKart (a small vehicle with an engine that kids can ride in). During your design phase, you must decide which fuel will power the GoKart. You are considering four fuels. First is gasoline, also known as octane, derived from petroleum. Second is also gasoline, but derived instead from wood pellets. Third, is natural gas, also known as methane. Finally, there is E85, which is mostly ethanol. (Photo of a child driving a GoKart is provided.)

Question	Question Intent
1. Which fuel would you use? Why? (list of fuels and each one's main chemical component is provided)	• Generate mental model of the scenario • Determine immediately accessible prior knowledge about the fuels and bases for decision-making • Determine participant's thinking on whether and how octane from petroleum vs. from wood pellets differ
2. Gasoline and E85 are liquids, while natural gas is available as a gas. Is this important? Why?	• Determine how the participant considers state of matter • Determine participant's thinking on how state of matter influences fuel usage, reactivity, outcomes, and consequences of use
3. E85 contains carbon, hydrogen and oxygen, while the other two fuels contain only carbon and hydrogen. Is this important? Why?	• Determine how the participant considers composition of matter • Determine participant's thinking about how composition influences structure, properties, reactivity, outcomes, and consequences of use
4. Are the molecular structures of the fuels important? Why? (ball-and-stick drawings, with element symbols added, are provided)	• Determine how the participant considers molecular structure • Determine participant's thinking about how molecular size, shape, and bonding/connectivity influence properties, reactivity, outcomes, and consequences of use
5. In terms of how the fuels affect the environment, is one fuel better than the others? Why?	• Determine what economic, environmental, social, political, ethical, and moral factors the participant views as important to consider in decision-making • Assess how student evaluates benefits and costs associated with the use of different fuels

Data Analysis. Individual interviews were audio-recorded and then transcribed. An iterative, non-linear constant comparison method of analysis was applied,[83] using web-based qualitative analysis software (Dedoose) to facilitate the analytical process. Two types of progress variables to track the development of understanding were considered: conceptual sophistication and modes of reasoning. Conceptual sophistication is a process of acquiring more sophisticated arrays of assumptions along with the knowledge of when those assumptions can be applied appropriately and is determined by the nature of students' underlying assumptions about the structure and properties of chemical entities and phenomena. Conceptual sophistication assumptions are primarily based on the participants' knowledge of chemistry concepts. The conceptual sophistication variable directly relates to participants' knowledge of the chemical domain and how they use that knowledge. Categorization of student assumptions was founded in work by Talanquer on commonsense reasoning in chemistry[25] as well as work on students' common alternative conceptions by Kind.[106]

Interview transcripts were first analyzed to identify the features noticed and used by different participants in making their decisions. These features were grouped into different categories such as “Common Use” (paying attention to the typical use of a substance in daily life), “Origin” (paying attention to the source of the fuel), “Molecular Size” (referring to the length of fuel molecules), or “Bonding” (referring to the number or types of chemical bonds present in molecules). An effort was made to identify the assumptions that the participants made while using these features in the decision-making process. These assumptions were grouped into various categories, for example: a)

Assuming that some feature associated with a fuel will hinder or facilitate its production or handling (e.g., storage); b) Assuming that a noticed feature will affect the environmental impact of the fuel; or c) Assuming that a noticed factor will affect the amount of energy produced by the fuel upon combustion.

All of the different elements used to characterize participants' BCR reasoning were ordered from least to most sophisticated, looking to identify and characterize different levels of sophistication in making decisions about what fuel to use. This process was guided by judgments of the extent and quality of the chemistry knowledge expressed and applied by study participants when making decisions. Once an initial set of levels was generated, study participants were assigned to the level that best represented their expressed BCR reasoning. This categorization effort led to a refinement of the identification and description of characteristic ways of reasoning at each level of sophistication.

To ensure inter-rater reliability, all transcripts were coded by at least two people. In this manner, codes generated by an individual in any given category (e.g., features, assumptions) were reviewed by at least one other individual. All discrepancies were discussed and resolved satisfactorily. This process allowed for the generation of a coding system that was consistently applied to all of the transcripts. A similar procedure was used to order different features from least to most sophisticated, and in assigning participants to different levels of sophistication.

Results and Discussion

Analysis of the types and number of features noticed and used to make decisions, together with the underlying assumptions and reasoning strategies applied by the participants when selecting the best fuel for a GoKart, allowed for the identification of different levels of sophistication in BCR reasoning. Similarly to the work of Clark and Linn,[24] participants seemed to fall into four major groups:

(i) *Intuitive*: making judgments based on everyday experiences and intuition

(ii) *Mixed*: relying on a combination of intuitive judgments and academic knowledge often used inappropriately

(iii) *Normative*: using academic knowledge to make judgments

(iv) *Nuanced*: integrating different aspects of academic knowledge to make decisions, paying attention to contextual issues

Major differences between each of these levels of BCR reasoning were detected along four major dimensions of analysis:

(i) *Fuel characteristics*: Refers to the properties or characteristics of substances that are used to make judgments and decisions, and to the reasoning strategies used to connect such properties with BCR issues.

(ii) *Potential impacts*: Refers to the potential impacts (e.g., environmental, health, economic, political) of fuel consumption that are considered and to how these issues are used to evaluate different materials and make decisions;

(iii) *Fuel availability and management*: Refers to those aspects of fuel production and distribution that are considered in evaluating different materials and making decisions;

(iv) *Energy production*: Refers to the extent to which differences in energy production for different fuels are considered to evaluate different materials and make decisions;

The distribution of participants into the four major levels of performance defined in this work is presented in Table 3-6, below. In general, participants with little or considerable training in chemistry tended to demonstrate, respectively, low or high levels of sophistication in BCR reasoning. The distribution of students in the intermediate stages of training was somewhat broader, although many of them demonstrated a "Mixed" level of sophistication. The boundaries between the different levels in BCR reasoning identified in the study were not sharp. Within any given level, participants who exhibited different degrees of sophistication can be found. One could thus expect to find individuals whose reasoning falls near the boundary between any two levels. However, the defined categories highlight four distinctive, from least to most sophisticated, approaches to BCR reasoning that can serve as a basis for developing strategies to facilitate learning in this area.

Table 3-6. Distribution of study participants among different levels of sophistication.

Educational Level	Number of Participants			
	Intuitive	Mixed	Normative	Nuanced
Freshman (F; N = 11)	8	3	-	-
Sophomore/Junior (SJ; N = 12)	2	8	1	-
Senior (S; N = 6)	2	3	2	-
Graduate (G; N = 5)	-	-	5	-
Professor (P; N = 5)	-	-	2	3

Intuitive BCR Reasoning. Close to one third of the study participants (12 of 39) exhibited an intuitive approach to BCR reasoning. Two thirds of these individuals were freshman chemistry students; no graduate students or chemistry professors fell within this category (see Table 3-6). Study participants placed at this level mostly relied on intuitive knowledge and ways of reasoning, rather than on chemical knowledge and thinking to make judgments and decisions. As illustrated by several of the examples presented in this section, these students often used affective impressions triggered by the names or the representations of different substances to make decisions. Their reasoning was constrained by an "affect heuristic"[56] in which positive or negative impressions prompted by words or images guided their judgments regarding benefits, costs, and risks, influencing their preferences and choices. The decisions made by these types of participants were also strongly influenced by their prior knowledge about or experiences with the different fuels included in the GoKarts instrument. Recognition of or familiarity with the name and effects of a substance were frequently used as main criteria to select or exclude options. Intuitive BCR thinkers tended to rely on relational reasoning, using vague associations between the name of entities and their expected properties (e.g., gases are dangerous, oxygen is good for us) to guide their thinking and justify their choices. The reasoning of these participants was highly sensitive to the information presented to them throughout the interview, as the recognition of some features triggered associations that led students to change their choices or question the appropriateness of their prior selections. In general, intuitive BCR reasoning was more reactive than proactive, and more hesitant than purposeful. Individuals at this level expressed few ideas of their own and mostly reacted to the information presented to them, expressing doubts about the validity or appropriateness of their judgments. Specific ways of reasoning expressed by individuals at this level are described below for each of the core dimensions of analysis.

Fuel Characteristics. Participants at this level considered a variety of properties or characteristics of substances to make BCR judgments and decisions. The characteristics most frequently used (by more than half of the individuals in this group) were: i) Known use and effects; ii) Origin; iii) State of matter; and iv) Chemical composition. In general, individuals at this level focused on these features one at a time and somewhat isolated from each other.

Students often referred to known uses or effects, or both, of the different fuels available for selection to justify their choices. As illustrated by the following interview excerpt, some students (4 out of 12) relied on the common use of a substance to select it:

Interviewer (I): *..., which one would you choose?*

F7: *(pause)... The gasoline from petroleum.*

I: *Okay. And why?*

F7: *Because that's what I put in my car I think.*

Common usage was sometimes used as indicative of wide availability, reduced danger, or greater effectiveness in the use of a particular fuel. In many situations (8 of 12), students referred to known effects of a fuel to either select it or exclude it. Consider this excerpt:

I: *...,which fuel would you choose?*

SJ10: *Um… gas is used in like modern day vehicles, and machines and such, I would probably go with the first one [gasoline from petroleum].*

I: *Okay, gasoline from petroleum? Is there any other reason?*

SJ10: *Um, for one I don't know, I always associated this one, the methane to be like harmful, so I kinda would avoid using that.*

In this case, octane from petroleum was chosen because of its common use and methane was excluded because of its perceived harmful effects. However, other students related methane with "less pollution" and used this association to choose this fuel as the best option. Familiarity with the use and effects of substances was used by all of the students at this level to discriminate between presented options and make a first choice, which some of them changed (5 of 12) as more information about the fuels was made available.

Knowledge or belief about the origin of the fuels was also an important influencing factor in the reasoning of individuals at this level (8 of 12). In particular, perception of a substance as natural led several students to favor it over other options:

F9: *I don't really know about the E85 but, I would just choose the natural gas. ... I remember in high school I knew that burning a whole bunch of stuff it releases all these toxins into the air, and then it destroys our ozone layer and stuff like*

> *that. So if we were to use a natural resource instead of like something that would make our atmosphere like not good, it would be better to use.*

Perception of the “naturalness” of the fuel’s source had a similar effect. This preference for “natural” materials was often justified with claims about their lesser impact on human health and the environment. This type of reasoning has been shown to influence BCR judgment in a variety of areas.[50,56]

During the interview, participants received information about the states of matter of the different fuels at room temperature. Over half of the students at this level (7 of 12) recognized the physical phase of substances as a relevant factor in the selection of the fuel. However, they often conceived physical state as a rather fixed property (not changeable), attributing specific properties, such as flammability or toxicity, to the particular state of matter rather than to the specific substance. The following excerpt illustrates this type of reasoning:

> **F5:** *Um, gas is probably more easily reactive, more easily lit than liquid.*
>
> **I:** *Can you explain to me what you mean by reactive?*
>
> **F5:** *Um (pause) gas will probably, once it's exposed to the air it will probably disappear, like react with the air or um, disappear so then it's not as visible either as liquid where you can actually see the chemical. Yeah.*

These types of students were able to recognize that the state of matter was relevant when thinking about fuel management issues, but frequently failed to differentiate between physical (e.g, diffusion) and chemical (e.g., reactivity) concerns.

Participants also received information about the chemical composition and molecular structure of the substances under consideration. All of the students at the intuitive level of BCR reasoning acknowledged some of this information as relevant for their decisions, but used it in rather naïve ways. Most of these participants seemed to conceive chemical substances as mixtures of elements rather than as chemical compounds, assuming that fuel properties would be determined by the properties of individual components (e.g., carbon, oxygen) and by their amounts (i.e., number of atoms) as represented in chemical formulas or molecular structures. This way of thinking about chemical substances is common among novice chemistry students.[7,107] Expressed ideas about the properties of chemical components were mostly based on naïve associations, such as thinking that carbon was somehow "bad" because of hearing that CO_2 polluted the environment, or considering oxygen as "good" because oxygen was somehow pure, better for nature, or easier to burn (oxygen was also seen as "bad" by some, because it was more flammable or could lead to more CO_2 production). The following interview excerpt illustrates this type of reasoning:

> **SJ10:** *..I mean I guess with this one having the oxygen, still probably makes it a safer option…*
>
> **I:** *When you say safer, what do you mean?*
>
> **SJ10:** *Um, safer in terms of like if it were to somehow come in contact with like, to, you know,....like would it be harmful.....um...because obviously, like, just like even in everyday like uses like if you were to like use gas for cars, it would, it would like, the fumes, the fumes it gives off are like not safe, you know what I*

> *mean? I don't know ethanol would make any difference in that, but just being that it contains oxygen makes me want to say that it is probably a little safer.*

The amounts of different components present in a chemical formula or a molecular structure were also used to make claims about the advantages of using one fuel over the other. Smaller molecular sizes were perceived by some as beneficial because they would lead to less CO_2 formed, or as less convenient by others because smaller particles would be consumed faster:

> **F4:** *Um...longer might mean that the fuel....lasts longer….Perhaps, or it has a different, um, different way of, efficiency maybe. Maybe that's like um, maybe a car runs longer, a longer time with octane than methane.*

The amount and diversity of components was also used as a cue to make judgments about how easy or difficult it would be to produce the fuel:

> **F1:** *Well, I would say that less is generally better because I'm guessing there are different processes for isolating the carbon, hydrogen and oxygen that would be used for each type of fuel. So I'm guessing this [ethanol] would need three processes and these [methane, octane] would need only two.*

The assumption that the size of or diversity of components in the molecules of a substance are indicative of how easy or difficult is to make it, or how favorable its synthesis may be, has been shown to be common among novice chemistry students.[108]

In general, participants at this level of sophistication tended to "objectivize" chemical substances, thinking of them more as objects than as chemical entities.[109] They compared fuels using features or properties commonly applied to differentiate between objects, such as functional usage and quality and amount of components.[110] Known or inferred fuel characteristics were used to make claims about potential impacts of using a given fuel and about difficulties in managing different types of substances.

Potential Impacts. The BCR reasoning of all of the students in this group was strongly influenced by their knowledge or beliefs about the environmental impacts of the different fuels under analysis. Only a third of these participants (4 of 12) also talked about potential effects on human safety. Only one of the students in the intuitive category referred to economic and political considerations. The views of intuitive thinkers about environmental effects were limited, mostly constrained to the production of CO_2 which was judged to be bad for the environment based on prior knowledge. These students talked about pollution in very general terms, and often made spurious claims about the effect of substances on environmental systems. Consider, for example, the following interview excerpt:

> **I:** *Can you explain to me what you think pollution is?*
>
> **F3:** *Um. That's a great question. Wow. So, uh, pollution I think would be when there's any emission of carbon dioxide, I think, in the air that would damage the ozone later, and that would be considered pollution.*
>
> **I:** *And where does that carbon dioxide come from?*
>
> **F3:** *Um...from the burning process of the octane and the methane I guess, like, carbon to oxygens? Wait. No...I don't know. That's a great question.*

In general, intuitive BCR thinkers expressed little knowledge about how pollutants may be generated. They knew that the use of different fuels led to pollution, but did not know much about the mechanisms for either pollution generation or pollutants' action on the environment. Their claims were mostly about which fuel would generate more pollution, or more dangerous pollutants, based on the analysis of fuel components (e.g., the fuel with more carbons in its formula will produce more CO_2; the fuel with more oxygen will likely be less damaging).

Fuel Availability and Management. Less than half (5 of 12) of the students at this level of BCR reasoning considered issues of fuel availability in their judgments. Those who did, mostly focused on issues related to abundance and perceived level of consumption of different sources. They were more inclined to select fuels from sources that were perceived as abundant or not being used as much as others. Some of the students in this category (8 of 12) also paid attention to some aspects of fuel management, mainly in the areas of fuel storage, transportation, and processing. Thinking about storage and transportation was triggered by information about the states of matter of the different fuels, while reasoning about fuel processing was motivated by the presentation of chemical formulas and structures. In general, individuals in this group thought that liquids were easier to store and transport than gases, and that substances with fewer components (e.g., C+H versus C+H+O) were easier to process.

Energy Production. Intuitive BCR thinkers did not consider energy issues when making judgments and decisions. Most of them did not seem to have an understanding of how combustion worked or how energy was generated through the burning of fuels. Some students acknowledged the need for oxygen in the burning process, but talked about it in the context of formation of CO_2 and not in terms of energy generation.

Mixed BCR Reasoning. Over one third of the study participants (14 of 39) expressed a mix of intuitive and academic ideas, the latter often spurious, when engaged in BCR reasoning. Over half of these students (8 of 14) were at the sophomore or junior levels in their undergraduate chemistry studies; no graduate students or chemistry professors fell within this category. Individuals at the mixed level of sophistication frequently relied on ideas and ways of thinking similar to those characteristic of the intuitive BCR thinkers, but their reasoning was enriched by academic knowledge about chemical substances and reactions. In some situations, academic knowledge was applied in combination with intuitive ideas, while in others cases students expressed "hybrid" conceptions in which chemical concepts (e.g., bond energy) were conceptualized in intuitive ways (e.g., the more bonds a molecule has, the more energy it will produce). Many of these participants often tried to apply chemistry knowledge that was not necessarily relevant to make judgments and decisions in the GoKarts task. They had a wider and richer chemistry knowledge base than students at the intuitive level, but their ability to apply such knowledge in proper, targeted, and productive ways was limited. These students paid attention to a wider set of fuel characteristics than intuitive thinkers and used them to make claims about potential impacts, fuel management and availability, and most distinctively, energy production. As observed in the case of intuitive BCR thinkers, many of these students were hesitant about their answers, were more reactive than proactive in the generation of ideas, and changed their fuel choice (7 of 14) as information was presented to them.

Fuel Characteristics. Similarly to individuals at the intuitive level of BCR reasoning, participants in the “mixed” category also considered features related to known use and effect, origin, state of matter, and chemical composition of the different fuels to make judgments and decisions. However, they paid attention to additional chemistry factors, such as the presence of specific functional groups in molecules, and types and quantities of chemical bonds in them.

As with intuitive thinkers, familiarity with known uses and effects of the different fuels under consideration played an important role in students’ BCR reasoning at the mixed level. Many students in this category also relied on vague recollections of environmental and safety issues to choose or discard a substance. However, they often made attempts to build causal links between expected properties of a substance and its chemical composition:

> **I:** *Okay so, you mention explosion from the octane and then combustion, okay so talk to me a little more about that.*
>
> **SJ1:** *Mmmm, I think they would just react quicker, I don't know why but I think with ethanol, it can sustain more than the rest of them. Well, I was kind of thinking of their chemical structures because octane is just carbon hydrogen bonds and then methanol has the OH, I mean ethanol has the OH attached to it, so it can sustain more for boiling and melting than the other ones. So I think those ones might be like the first ones to blow up or something as opposing to the ethanol, which would take more to do.*

In this case, the student was trying to relate the composition and functionality of ethanol to its potential reactivity (facility to explode). As was common among participants at the mixed level, this student was seeking to apply chemical knowledge to justify claims or choices, but the arguments were frequently incomplete, as in the above example, incorrect, or somewhat irrelevant to the problem under consideration.

Considerations about the origin of the fuel were also important for this group (9 of 14). However, beliefs about the intrinsic goodness of natural substances were less prevalent than among intuitive thinkers, and references to issues of fuel availability and management were more dominant (e.g., more abundant source, renewable source, easier to obtain). Similarly, almost all of the students in this group (13 of 14) referred to the state of matter of fuels as a relevant property to consider, mostly in relation with fuel management but also for energy production. Attention to chemical composition was also substantial, with arguments mostly focused on the nature and amount of different components. The assumption that the properties of the individual components determine the properties of the chemical compound was still pervasive, but properties discussed were linked to specific ideas about how those properties affected the combustion process. For example, some students thought that the presence of oxygen would make ethanol more combustible:

> **I:** *So you said the oxygen might make it more combustible?*
>
> **F8:** *Yeah, cause you don't, that's why you see* O_2 *tanks like, don't go, don't put near flames, very flammable, because it's easily combustible.*

Others, who recognized the presence of specific groups of atoms in molecules (5 of 14) often made claims about how these functional groups could alter the combustion process:

> **I:** *Mhm. Why would ethanol work best?*
>
> **SJ4:** *Because it could react with other things that have OH groups and NH groups, and it could, I think it would have a cleaner, the reactions would probably be…they could potentially be cleaner than the reactions of octane or methane where you might have, in the other ones you might have harmful side um products as well as the energy, and the OH would probably yield less of those harmful uh byproducts.*

In this case, the student seemed to claim that substances with OH are somehow "cleaner" or less harmful than others. This last example illustrates how some students often "hybridized" their chemical knowledge with intuitive ideas about the nature of chemical substances (oxygen-containing entities seen as clean, not harmful chemical substances).

Students in this group also used state of matter, chemical composition, and structural features such as number (4 of 14) and types (3 of 14) of chemical bonds, to make claims related to energy production (students' ideas described below under "energy production").

Potential Impacts. BCR reasoning for most of these participants (12 of 14) was also dominated by concerns about the environmental impact of using the different fuels. However, more than half of these students (8 of 14) referred to human safety issues. In particular, there were judgments about the relative flammability and facility to explode of the substances under consideration. Arguments about environmental and safety impacts tended to be weak, as students relied on generic associations (e.g., gases are more flammable and explosive than liquids, CO_2 is bad for the environment) to justify their choices. Some students recognized CH_4 and CO_2 as greenhouse gases, but they expressed misunderstandings about their role in the atmosphere (e.g., referring to the action of these gases on the ozone layer). Only one of the students in this category considered political implications of relying on one fuel over others.

Fuel Availability and Management. References to the availability of fuels among this group of students (6 of 14) were similar to those observed among intuitive thinkers. However, some of these participants (4 of 14) referred to the renewability of fuel sources as an important factor in their choice. Although introduction of information about states of matter triggered ideas about fuel storage (4 of 14) and transportation (3 of 14), as was the case for intuitive thinkers, the physical state of substances led several of these students (5 of 14) to consider issues of “reaction control.” In particular, students discussed how state of matter would affect the ability to control explosions and the burning process. Several participants at the mixed level (5 of 14) also referred to differences in fuel processing. However, rather than focusing on effects of chemical composition on ease or difficulty of producing a fuel, as intuitive thinkers did, mixed thinkers mostly focused on how different fuel sources would facilitate or hinder fuel production.

Energy Production. While intuitive BCR thinkers did not pay attention to energy issues in their selection of the best fuel, and most of them had little understanding of the burning process, participants at the mixed level often made many references to factors affecting energy production and the combustion process. They referred to factors such as energy costs (5 of 14), energy produced (6 of 14), and energy content (6 of 14) for the different fuels. Most individuals recognized that energy was generated as a result of a combustion reaction, although their understanding of such process was, in most cases, incorrect or incomplete. Students in this category often linked physical or chemical features of the different substances with the amount of energy required or produced during combustion. However, student thinking about chemical energy was naïve, based on an assumption that chemical bonds contain energy that is released when the bonds are broken. This type of thinking has been elicited by many authors and has proven difficult to change through traditional instruction.[106,111] Within this view, one can expect students to assume that the more bonds in a molecule, the larger the amount of energy produced. The following excerpt illustrates this type of reasoning:

> **S5:** *Maybe the smaller they are it's easier to burn them. It takes less time.*
>
> **I:** *Why is that?*
>
> **S5:** *Cause it's easier to like break the bonds....*
>
> **I:** *Of a smaller molecule?*
>
> **S5:** *Yeah. But they can release less energy, so.......*
>
> **I:** *So breaking the bonds releases energy?*
>
> **S5:** *Yeah.*

In this example, the student is struggling to decide between competing intuitive ideas about the burning process: smaller molecules are easier (faster) to burn, but they produce less energy. Other students struggled with other competing ideas, such as assuming that smaller molecules require less energy to break apart, or produce less CO_2 (less pollution), but they also generate less energy. Some of these participants also expressed misunderstandings about energy exchanges, such as believing that if more energy is invested in burning a fuel, more energy will be released upon combustion:

> **SJ7:** *I think given this information I might choose the natural gas...well, I think I would probably still stick with the gasoline from wood pellets because it would require more energy to combust it, the gas would be more easy to combust, so that might make it......less of an energy output.*

Besides these different issues related to students' intuitive reasoning about chemical energy, participants at this level also relied on unproductive strategies to compare inputs and outputs in the combustion process (e.g., energy released; amount of CO_2 produced), paying little attention to the specific constraints of the system under analysis (i.e., fuel tank with a fixed volume). Evaluations were made by comparing one single molecule with another (as represented in the images presented during the interview), without ever questioning whether other approaches (e.g., comparing fuel samples of equal mass) would be more appropriate.

Normative BCR Reasoning. Over one quarter of the study participants (10 of 39) relied on both their general academic knowledge in chemistry and their specific knowledge about the fuels under consideration to make judgments and decisions. Half of this group was graduate chemistry students; the rest were junior and senior undergraduates and chemistry professors. There were major qualitative and quantitative differences between the knowledge and ways of thinking expressed by individuals at the normative and mixed levels of BCR reasoning. For the most part, participants at the normative level applied scientifically correct chemical knowledge that was relevant to the task at hand. They demonstrated a relatively broad knowledge base about fuels, their production, properties, and effects, and they proactively recalled information and generated ideas that allowed them to differentiate one fuel from another. They paid attention to contextual factors in making judgments and recognized the need for more information (e.g., heat of combustion values) to make more definitive decisions. Almost all of the individuals in this group (9 of 10) started the decision making process by weighing several factors before settling on a particular fuel option, which remained practically unchanged during the interview. However, they frequently evaluated pros and cons of different alternatives based on various criteria (e.g., energy vs. amount of CO_2 produced), and recognized that their choice could be different if they changed the weight given to some factors over others (e.g., safety over engine power) or had access to additional data. In general, these participants built clear causal links between fuel characteristics and potential impacts, availability and management issues, and energy production.

Fuel Characteristics. As in other levels, participants at the normative level of BCR reasoning also paid attention to fuel characteristics related to known use and effects, origin, state of matter, and chemical composition and structure. However, they expressed more extensive and sophisticated knowledge about relevant features than individuals at the mixed and intuitive levels. They often considered more than one factor at a time when making evaluations, as illustrated by the following interview excerpt:

> **G3***: ….all these are gonna produce greenhouse gases so in some sense you are not eliminating that possibility, so gasoline whether you get it from petroleum or wood pellets, is still gonna be the same, … the only difference between those two is where you're sourcing it from, so wood pellets you can say it's a sustainable resource, so gives it an edge over from petroleum but in the end … you're not getting any benefits. Natural gas, it is still a non-renewable resource but on the exhaust side, it's gonna be better than gasoline… ethanol…I don't think it's very efficiently produced… if produced from corn it's not economical or environmentally sound as much as we'd like to think … on the exhaust side I think you're still gonna produce* CO_2*. …I think that on the exhaust side, the methane, natural gas will give you a better environmental footprint.*

In this case, the graduate student was trying to weigh issues related to origin versus environmental effects of the fuels under consideration. This excerpt also illustrates the ability of participants at the normative level to recognize that judgments and decisions depended of a variety of factors that were not defined in the GoKarts probe, such as the source used to produce ethanol (e.g., corn vs. sugar cane vs. biomass) or the nature of the process needed to generate octane from wood pellets (which could be energetically and environmentally costly).

Normative BCR thinkers considered physical (e.g., states of matter) and chemical (e.g., chemical composition and structure) characteristics in ways that reflected a deeper understanding of the properties and transformations of matter. For example, several of these individuals (6 of 10) recognized that natural gas could be pressurized or liquefied (or that liquids may need to be vaporized to combust), and discussed the energy costs or safety issues that such processes could generate. Similarly, all of them noticed differences in chemical composition and structure, but most claims in this area focused on the effect of these factors on the nature of the products of the combustion reaction (e.g., long hydrocarbon chains may generate more diverse byproducts, ethanol combustion may result in fewer free radicals). None of these individuals looked at the properties of chemical substances as resulting from the weighted average of the properties of their individual components (i.e., C, H, O). Few of them (4 of 10) paid attention to the number of bonds in a molecule to make predictions about energy production, although misunderstandings in this area (3 of 10) were still detected.

Potential Impacts. Most of the participants at the normative level (9 of 10) considered environmental impacts in making their decisions. Half of the people in this group referred to human safety issues, and two of them expressed economic and political considerations. Arguments about environmental issues were less definite than those generated by individuals at the intuitive or mixed levels, who tended to think of substances as either good or bad. Normative BCR thinkers recognized that outcomes would depend on diverse factors, such as the nature of the source (e.g., corn versus biomass) and the process used to produce the fuel. The judgments and decisions of these individuals were also responsive to the particular context defined in the GoKarts task, as illustrated by the following interview excerpt:

> **S7:** *Because from burning ethanol it's going to be cleaner. Because it's an amusement park many of the players are children. So you don't want to burn*

> *petroleum which can contaminate the room… Ethanol, I think it's better because even though it costs the same, but it burn out like much cleaner. The methane is a gas, so it's harder to contain and fill. …I would guess ethanol would cost more. But even when they cost the same I would choose ethanol because it's environmentally safe because you can drink it.*

This student's evaluation of the potential impacts of the different substances was influenced by the recognition of the specific intended use of the available fuels.

Fuel Availability and Management. Concerns about fuel availability among individuals at the normative level were mostly related to issues of renewability (6 of 10) of fuel sources. Most (9 of 10) discussed pros and cons in terms of fuel storage and, most distinctively, most (9 of 10) engaged in analyses related to fuel processing. Many of these participants expressed that the nature of fuel production would have a strong influence in their decision, as such process would determine energy costs and environmental and safety impacts.

Energy Production. All of the participants at the normative level expressed a clear understanding of the combustion process. Most of these individuals (8 of 10) referred to differences in the amount of energy released upon combustion as a factor to consider in making decisions. However, many recognized that other competing factors needed to be taken into account, such as the energy invested in producing the fuel, the amount of CO_2 produced per unit of energy generated, or the efficiency of various types of engines. Although normative BCR thinkers recognized the role of chemical composition and structure in determining energy of reaction, few (3 of 10) attempted to make predictions based on these features. They were more likely to refer to the need for experimental data to make a decision.

Nuanced BCR Reasoning. Only 3 of the 39 total participants in the study were judged to fall within the “nuanced” level of BCR reasoning. All of them were professors of chemistry. As was the case for individuals at the normative level, these participants properly and productively applied their disciplinary knowledge in chemistry and their specific knowledge about fuels to make judgments and decisions. From this perspective, the description of core knowledge and ways of thinking presented in the previous section also applies to nuanced thinkers. However, individuals in this category expressed and applied their knowledge and reasoning in more integrated ways than participants at the normative level. Their analyses were richer and more nuanced, often based on the consideration of various conditions or scenarios that could lead to different decisions. Consider the following example.

> **I:** *Okay, so what environmental impacts are you thinking about?*
>
> **P4:** *I’m thinking primarily about greenhouse gas emissions. Because we have declared these go-kart engines have catalytic converters so you can ignore the* NO_x *problem, um, I mean, I'm biased because I'm thinking about the environmental impacts to consider, if we expand the definition of environmental to include fields of corn, forests that need to be cut down for wood pellets, if but this is for a small fleet of GoKarts so I'm not sure that that's a significant concern. Again, I've rambled about the ethanol problem … that ethanol from corn as a national policy is a horrible way to go but for powering a fleet of GoKarts, I don't*

> *see that as being a large component......if we are assuming that fueling stations are leak tight, I don't see much large impact for any of these things to be honest, but if I'm talking about a scale, I guess I'm only really concerning myself with* CO_2 *output.*

This excerpt corresponds to the interview of a participant who, before making a decision, had already engaged in defining the conditions under which he would assume the GoKart engine would work: it would have a catalytic converter, to reduce NO_x emissions, and it could work at low temperatures, which would allow it to run with oxygenated compounds. At this stage, he was evaluating potential environmental impacts, not only trying to define the scope of his analysis, but also recognizing the limitations in his reasoning. In general, nuanced thinkers expressed very detailed knowledge about the systems and phenomena under consideration, and promptly acknowledge the scope and limitations of the claims they were making. Many times their knowledge manifested in the form of simple rules or associations (e.g., oxygenated compounds burn at lower temperatures; oxygenated compounds have higher oxidation states), but they were able to generate rich mechanistic explanations when prompted.

Synthesis of Results. Analysis revealed substantial differences in the knowledge, assumptions, and modes of reasoning applied by the study participants to evaluate the benefits, costs, and risks of using different fuels in the GoKarts scenario. Major differences along core dimensions of analysis for individuals with different levels of sophistication in BCR reasoning are summarized in Table 3-6 on page 96. The findings elicit domain-general differences, which are likely to characterize the BCR reasoning of people in different contexts, and domain-specific differences, which are tightly linked to the actual focus of the research task (i.e., selection of the best fuel for a GoKart). At the domain-general level, results confirm the central role that affective impressions play in judgment and decision-making in authentic contexts for novice learners or individuals with limited knowledge.[56,59] Intuitive BCR thinkers in this study often relied on an affect heuristic that was triggered by level of familiarity with the entities under analysis, perceptions of risk or lack of control, and preference for what is natural. These intuitive responses were strongly influential in the decisions made by two thirds of the study participants (intuitive and mixed thinkers), including the majority of the undergraduate students who were interviewed.

At a general level, the results also support the suggestion that the transition toward more expert knowledge and ways of reasoning often entails the development of hybrid or synthetic constructs, involving the merging of intuition and disciplinary concepts.[24,112] A large fraction of the students who had completed college chemistry courses beyond the introductory level expressed these types of ideas. The knowledge base of individuals with higher levels of training in the discipline was certainly broader than that of freshmen, but the ability to apply such knowledge in proper and productive ways was mostly confined to those participants with substantial chemistry training (i.e., graduate students and professors). The comparison of mixed and normative forms of reasoning suggests that the transition from one level to the other demands considerable pruning and refinement of concepts and ideas, and significant reflection on the context of their application. Similarly to findings in other areas,[24,113] higher levels of sophistication in BCR reasoning in this study were characterized by a wider and stronger integration of knowledge, a higher ability to recognize and weigh the effects of several variables, a greater attention to tradeoffs in decision making, and a more focused consideration of the specific goals and constraints of the task at hand. Intuitive and mixed thinkers in the sample were more likely to rely on non-compensatory decision-making strategies, in which options judged to be unacceptable under certain criterion were simply eliminated, while normative and nuanced thinkers used compensatory approaches, in which benefits and drawbacks were more systematically weighed. These differences in decision-making reasoning between less and more advanced students have been observed in other scientific disciplines.[114,115]

This study also revealed major domain-specific differences between study participants. Reliance on chemistry knowledge and ways of thinking was minimal among individuals at the intuitive level. On the other hand, students at the mixed level often tried to apply many chemistry concepts or ideas that were not necessarily relevant, appropriate, or productive for making the required judgments and decisions. Their expressed ideas revealed basic misunderstandings about the nature of chemical substances and processes. In particular, many of these students seemed to hold a “compositionist” view of matter, in which properties of substances are seen as the result of the weighted average of the properties of their individual components (i.e., elements, atoms, bonds).[116] Within this perspective, chemical compounds whose molecules have, for example, more oxygen atoms would be seen as more flammable; and molecules with more chemical bonds would be judged as richer in energy (with chemical bonds seen as containers of chemical energy). This conceptualization of substances had a strong influence on the decisions made by many of the undergraduate chemistry students who participated in the study, and remnants of this way of thinking were detected in the reasoning of several advanced students.

Attention to compositional and structural features of the chemical substances under consideration somewhat decreased among individuals at the normative and nuanced levels. These participants seemed to recognize limitations in making reliable inferences based on compositional and structural information, and often referred to the need for actual experimental data, such as heats of combustion, to make more definitive claims in particular contexts. The recognition that other types of information, beyond what was provided in the GoKarts probe, were needed to make better judgments and decisions was characteristic of individuals at the more advanced levels of sophistication in BCR reasoning. These participants also took advantage of their knowledge base in different areas of expertise to make their decisions. The ways in which knowledge and information about the chemical substances under evaluation was used by individuals at different levels of sophistication in BCR reasoning was clearly distinct. While intuitive and mixed thinkers tended to focus on fuel characteristics seeking to infer potential impacts of their use, normative and nuanced thinkers paid closer attention to issues related to the production of such substances.

Conclusions

The results of these studies suggest that a large fraction of college students complete their chemistry degrees, or undergraduate chemistry courses required by their major of study, without reaching normative levels of BCR reasoning in chemistry contexts. Their ability to make productive judgments and informed decisions in many relevant situations in their personal and professional lives will likely be limited. Current curricular approaches and teaching practices in chemistry at the undergraduate level offer few opportunities for students to apply and integrate their knowledge in tasks that, like the GoKarts probe used in this study, demand evaluation of the benefits, costs, and risks of different alternatives. Despite well-substantiated educational benefits of activities that are more active, constructive, and interactive,[117] college chemistry courses are characterized by their focus on passive forms of learning. Building reasoning capacity takes concerted effort over years,[8] thus isolated educational interventions in some chemistry courses are likely to have little impact.

Contributions to Knowledge

Significant improvement in BCR reasoning demands ambitious and coordinated changes in chemistry education.[65,110] In particular, the results of this study suggest that there are two transitions that could be aided by deliberately planned learning activities that occur in a coherent manner across the curriculum. First, the transition from intuitive toward more advanced reasoning requires a shift from reliance on recognizable surface features (e.g., familiarity) and affect heuristics (assignment of "goodness" or "badness") toward noticing relevant chemical characteristics (e.g., reactivity under different conditions) and processes (e.g., different reaction pathways). Second, the transition toward more normative reasoning seems to demand recognition of limitations of model-based explanations, greater emphasis on data-driven decisions, and specification of trade-offs. Interventions likely to be useful could include investigation of messy problems in which data from different areas must be considered and integrated, and problems in which different scientific models that could be used to explain results and predict behaviors have limitations that need to be recognized and evaluated. Other authors have shown that engaging students in the invention of their own alternatives to address complex issues fosters the development of more sophisticated decision-making reasoning.[118] Similarly, explicit training in decision-making strategies seems to improve the quality of science students' judgments and choices.[115]

Future Work

Findings support the calls to reform chemistry education at the postsecondary level in ways that better promote the integration and application of knowledge in realistic settings.[119,120] At a first level, students need help building a more robust and coherent knowledge structure on which they can rely when making decisions; this will demand a careful reconceptualization of chemistry curricula to better support knowledge integration.[110,121] Additional research on and development of learning progressions for core disciplinary ideas and practices is desperately needed to better scaffold student learning at the college level. Second, there is a need to transform teaching approaches to create opportunities for students to apply and construct knowledge as they engage in exploration, design, and evaluation activities focused on fundamental and relevant matters.[66] Finally, assessment practices must be revised to move beyond the mere evaluation of factual content knowledge and algorithmic reasoning, and better probe student knowledge and reasoning in authentic contexts.[122]

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CHAPTER 4

USE OF EYE TRACKING TO UNDERSTAND STUDENTS' INTERPRETATIONS OF STRUCTURE-PROPERTY RELATIONSHIPS IN THE CONTEXT OF GLOBAL WARMING

In a nightmare world, we would perceive the world around us as being continuous and without structure. However, our survival as a species has been possible because we have evolved the ability to 'cut up' that world mentally into chunks about which we can think and hence give meaning to.

-- John K. Gilbert[1] –

Introduction

Gilbert's quote can be taken as an elegant, albeit simplified, explanation of how and why people interpret representations of the natural world. This chapter will explore the importance of visualizations in chemistry, namely molecular structures, and attempt to provide a better understanding of how students relate these visualizations to chemical phenomena.

Visualizations in Chemistry

Chemistry is a highly visual science.[2,3] Chemists use a multitude of representations to symbolize atoms, molecules, chemical processes, and data. These representations range from symbols and icons to molecular models, chemical structures, formulas, and equations.[4]

Visual representations can be either internal (an archetype constructed by the learner) or external (presented to the learner).[5,6] Chemists are apt to use both types of representations – internal representations as mental images of their own understandings of complex concepts and principles and external representations (e.g., drawings, equations, and graphs) as a means of communicating with other chemists, students, or the general public.[7]

There are numerous examples in the literature noting the importance of external representations in promoting student learning and understanding. External representations have been shown to be (i) important for constructing knowledge,[8] (ii) valuable for communicating and integrating scientific concepts,[9] and (iii) able to support a flexible understanding of scientific phenomena.[10] Additionally, some studies indicate that students with high visuospatial abilities also have higher problem-solving skills in science[11] and a deeper understanding of chemistry.[12–17] In chemistry and physics, it has been shown that an understanding based on external representations is most often determined by the surface features of the representations themselves, such that learners struggle to associate these surface features with deeper conceptual explanations.[14,18–24] Some students treat the visualizations as qualitative only, choosing to solve problems quantitatively even when it is not necessary.[25] In other words, students tend to pay more attention to the symbols themselves instead of what the symbols represent. Thus, difficulty recognizing and interpreting the representational language of chemistry can often be a hindrance for chemistry students.[26,27]

Structure-Property Relationships

As part of learning the representational language of chemistry, a fundamental skill in chemistry is to predict macroscopic properties of molecules based on their respective microscopic structural representations. In fact, many authors have noted the importance of learning to predict properties of substances based on their representations, be it macroscopic, sub-microscopic, or symbolic.[21,22,28–30] “Structure and Properties of Matter” has been identified as a disciplinary core idea (PS1.A) in the *Next Generation Science Standards* for K-12 education in the United States.[31] In their Chemical Thinking Learning Progression, which is the framework of the research presented in this chapter, Sevian and Talanquer define *Structure-Property Relationships* (SPR) as a core chemistry concept that is invoked whenever the following essential question is asked: “How do we predict the properties of materials?”[32]

Despite the importance placed on this disciplinary idea, SPR is a challenging concept to grasp for students at all levels.[33,34] The difficulties students encounter with SPR have been the subject of a vast amount of literature in chemistry education. Special attention is paid here to the instances that are most relevant to the work presented in this chapter. The most common problems among students seem to be:

1. A reliance on heuristics[†] to reduce the number of factors to be considered when reasoning about SPR.[19,35–38]
2. An assumption[†] that the properties of a substance are a result of linearly adding the properties of the parts of the substance. Talanquer refers to this as *additivity*.[37,39]
3. A belief that the properties of a substance at the microscopic level are simply a smaller scale version of the properties observed at the macroscopic level (e.g., copper atoms are red because copper metal is red).[37,40–42] Talanquer refers to this as *inheritance thinking*.[37]
4. A general inability to reason about substances and processes at multiple spatial scales simultaneously.[21,22,33,43–45]

While there is no shortage of literature on students understandings and misconceptions of how they *think* about SPR, there is a lack of quantitative measures that relate these understandings and misconceptions to viewing behaviors of molecular structures. This study aims to fill that gap by exploring the use of eye tracking technology.

Eye Tracking

The study described in this chapter employed the use of eye tracking, a method of recording an individual's eye movements, in order to uncover underlying cognitive

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[†] The reader is referred to Chapter 3 for an explanation of heuristics and assumptions.

processes. Common eye trackers use a light source, typically near infrared, to illuminate the eye, creating corneal reflections that can then be captured by a camera. The images captured by the camera are used to determine angles of reflection of the light source on the cornea and pupil which are then used to calculate the point of the participant's gaze.[46]

Eye tracking is relatively new to the field of chemistry education, with only a handful of studies having been published at the time of this writing.[47–54] Tang and Pienta have used eye tracking to investigate the role of complexity factors in both stoichiometry[52] and gas law[50,55] problems. Williamson et al.[53] used eye tracking to explore how students used ball-and-stick images versus electrostatic potential map images when presented with different types of questions about a molecule. Stieff et al.[54] examined students' representational competence when looking at interactive animations used in molecular mechanics. These studies differ from this work because they were designed to investigate where and how long participants looked and related this information to how they answered the respective questions.

Outside of chemistry education, it has most often been employed for usability studies,[56–60] reading research,[61–65] and visual search tasks.[66,67] Measurements of eye movements are thought to be a good representation of visual attention. Hoffman and Subramaniam[68] have shown that if an individual's eyes are focused on an object, their attention is also on that object. Additional literature has shown that underlying cognitive processes can be uncovered with eye movement data.[69–72] This research relies on two underlying assumptions: the *immediacy assumption* and the *eye-mind assumption*.[69] The immediacy assumption states that the viewer begins processing the information being fixated on immediately and before moving to the next fixation. With each new fixation, the viewer processes a different region of the information being presented. The eye-mind assumption states that a link exists between the eyes and the mind such that whatever the eye fixates on, the mind processes. Thus, fixation time is indicative of processing time.

In order to begin to productively discuss eye tracking, it is important to understand some common terms associated with eye movements and eye tracking research:

- A *fixation* is a pause in eye movement indicative of attention focusing on a stationary visual object.
- *Fixation duration* is the length of time for a specific fixation before the viewer moves on to another visual region of interest.
- *Total fixation duration* is the sum of the fixation durations for every fixation within an area of interest.
- A *saccade* is the rapid movement of the eye between fixations.
- An *area of interest (AOI)* is a researcher-identified region of the visual stimulus in which the researcher is interested in collecting eye movement data.
- An *eye fixation sequence* is a participant’s sequence of fixations among AOIs.

These terms will be used throughout this and the subsequent chapter, however they do not represent an exhaustive list of terms related to eye tracking and their operational definitions may vary among different research studies.[‡]

[‡] Expanded lists of terms and additional definitions are available elsewhere.[47,75,93,98]

Research Questions

Students' understandings of structure-property relationships have been studied extensively. However, an examination of how these understandings relate to what the students' visual and cognitive focus is on has yet to be explored. To that end, this study aims to address the following research questions:

1. What does examination of eye gaze patterns reveal about chemistry students' understanding of structure-property relationships when presented with molecular structures and infrared (IR) spectra?
2. In what ways do the understanding, interpretation, and assimilation of information in molecular structures and IR spectra vary for students at different levels in their chemistry education?

Methodology

In order to answer the research questions of this study, a mixed methods approach, combining both qualitative and quantitative methodologies,[73,74] was used. Quantitative data were collected via an eye tracking system that tracks a participant's gaze on a visual stimulus. Concurrently, qualitative data were collected via a think-aloud protocol. The methods were designed to elicit student thinking about molecular structures and IR spectroscopy in the context of global warming. The use of IR spectroscopy and the global warming context were selected because it allowed for the examination of how students explain properties (i.e., IR activity) that are directly related to molecular structures in a scenario in which they would have to apply that explanation in a larger context.

Setting and Participants

Study participants were recruited from a medium-sized non-traditional university in the northeastern United States during the Fall 2014 semester. Undergraduate student participants were recruited from their chemistry courses with the approval of the course instructor. Graduate students were recruited via a chemistry graduate student email distribution list. Recruitment efforts, as well as the methodology, were approved by the university's Institutional Review Board. Freshmen and seniors received nominal extra credit from their instructors as compensation for participation. Sophomore and graduate students received small denomination gift cards as compensation for their participation. Table 4-1 shows the distribution of participants by chemistry educational level.

Table 4-1. Distribution of participants by chemistry educational level.

Chemistry Educational level (Abbr)	**N**	**Course Enrolled In**
Freshman (F)	9	General Chemistry II
Sophomore (S)	7	Organic Chemistry I*
Senior (SR)	4	Final year of studies
Graduate Student (GS)	6	--

**Participation in this study occurred after the unit on IR spectroscopy.*

Eye Tracking System

Eye movements were monitored with a Tobii X2-60 remote eye tracking system mounted to a 22-inch (measured diagonally) Dell monitor with a resolution of 1680 × 1050 pixels. The Tobii system uses an improved version of a technique called Pupil

Centre Corneal Reflection (PCCR). PCCR uses near infrared illumination to create reflection patterns on the cornea and pupil of the eye of the user. Two image sensors are used to capture images of the eyes and the reflection patterns. The software then uses advanced image processing algorithms and a physiological 3D model of the eye to estimate the position of the eye in space and the point of gaze. The system has a sampling rate of 60 Hz, thus the participant's gaze data was collected approximately every 16 ms. All participants were calibrated using a nine point calibration before the beginning of each eye tracking session.

Tobii Studio 3.2.3 was used to build the eye tracking protocol, operate the eye tracking hardware, and collect the eye tracking data. For each eye, the software collects and reports the following data:

- *Time (μs)* – Timestamp of a gaze data recording obtained from the eye tracker firmware clock
- *Eye position (mm)* – X, Y, and Z coordinates of the 3D position of the eye relative to the UCS (User Coordinate System) origin point on the eye tracker.
- *Pupil diameter (mm)* – scalar measure of the participant's pupil
- *Validity code* – Confidence level that the eye has been correctly identified. Integers range from 0 (high confidence) to 4 (eye not found).
- *Gaze point (pixels)* – X and Y coordinates of the gaze point on the media element

Data Collection

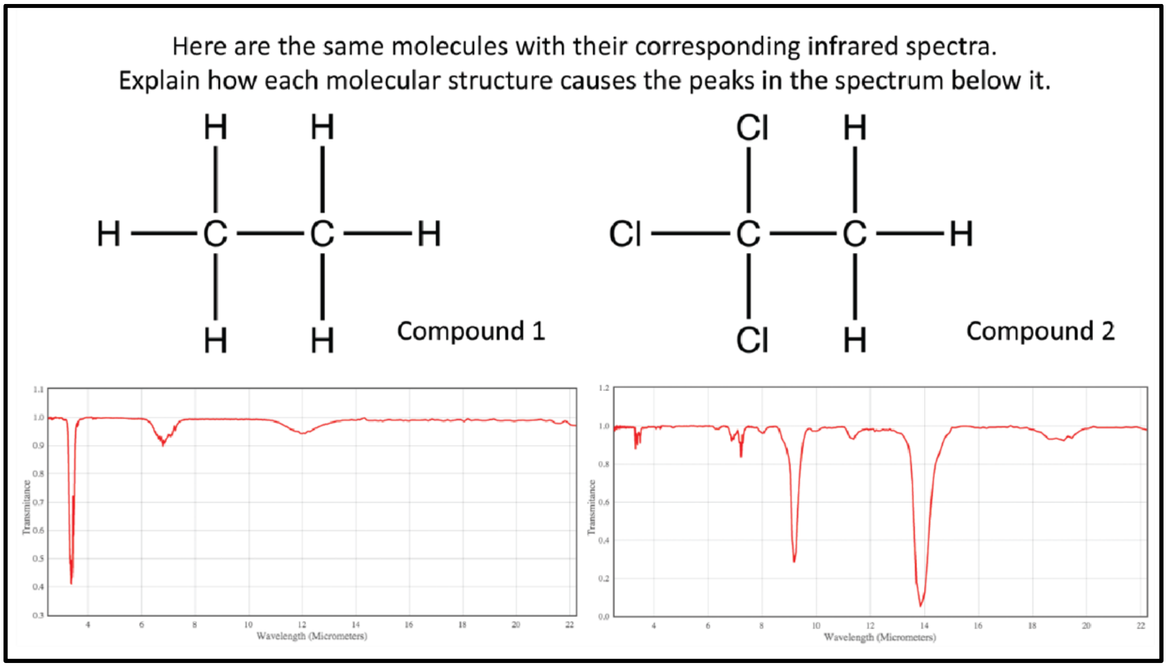
While eye tracking creates a quantitative record of where participants are looking, it is not necessarily a reliable indication of what they are thinking. Thus it is common during eye tracking protocols to use methodological triangulation to enhance confidence in the reported findings.[75] Methodological triangulation refers to use of more than one methodological approach when investigating a research question.[76–79] For this study, a think aloud protocol was used concurrently with eye tracking in order to capture participants' working memory responses directly. While cognitive interviewing would have been preferred, it has been shown that verbal interaction with a participant during tracking may alter his or her eye movements.[80]

Think aloud protocols have been used by previous authors in conjunction with eye tracking for investigating perceptual and attentional processes,[81,82] cued retrospective reporting,[49,57,83] and investigating the relationship between vision and speech over time.[84] The advantages of concurrent verbalizations are that (i) the data sources are recorded simultaneously, and can thus be closely linked[75] and (ii) the protocol provides an in-the-moment perspective, which has been shown to deviate from a retrospective approach.[89] Several authors have also noted that the use of concurrent verbalizations can prove problematic, particularly that (i) the participant performs the task slower[85,86] and (ii) the increased cognitive load slows down eye movements and learning processes.[87,88] Because this study does not rely on processing time or speed of the task, it was decided that the advantages of using a concurrent think aloud method outweighed the problems.

Procedure

Upon arrival at the eye tracking lab, students were given an overview of the research study and a description of what participation would entail. After signing the consent form, students were given an explanation of the "think aloud" protocol.

During the eye tracking session participants were asked to answer questions about the relationship of two compounds to their respective IR spectra (Figure 4-1). As the question of the instrument was open-ended, participants were not restricted to a pre-specified amount of time that they could view the visual stimulus. The researcher had control over advancing the slide and chose to do so when the participants indicated that they had provided as complete an answer as they thought possible.



Here are the same molecules with their corresponding infrared spectra.
Explain how each molecular structure causes the peaks in the spectrum below it.

Figure 4-1. The visual stimulus shown to participants during the eye tracking part of the study. IR spectra were obtained from the NIST Chemistry WebBook (http://webbook.nist.gov/chemistry/).

Data Analysis

The instrument was designed so that the participant is asked to use the structure in order to explain the IR spectrum associated with it, thus explicitly eliciting SPR thinking.

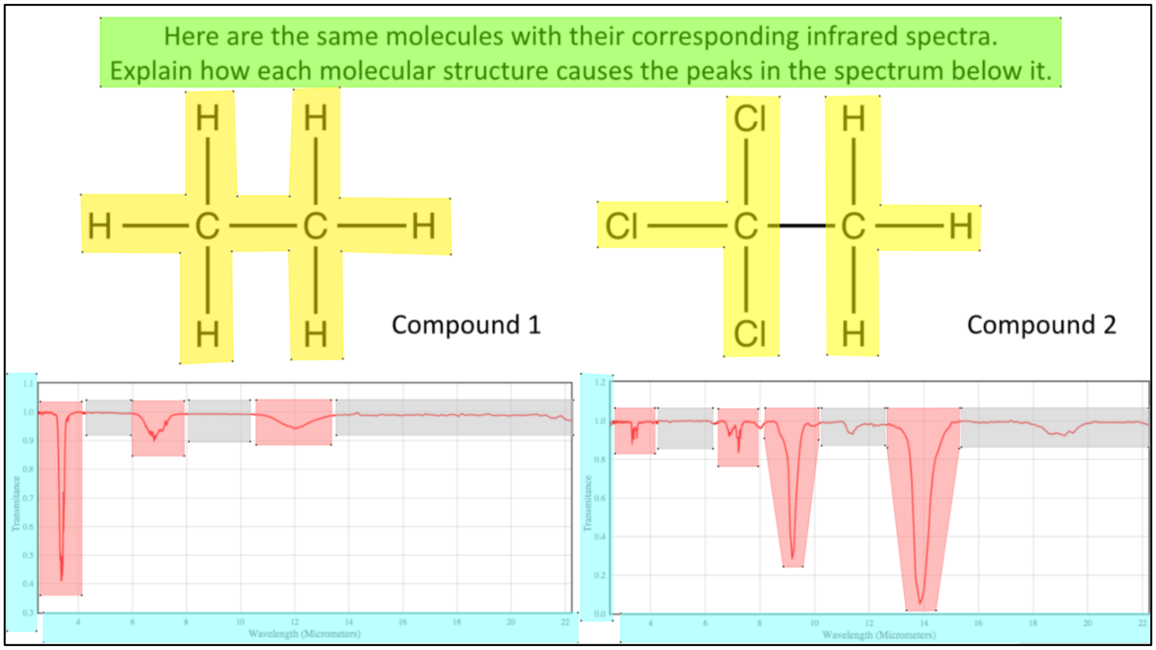
Qualitative Analysis. Audio recordings of the participants' think aloud sessions were first transcribed to text. The text was qualitatively coded[90] by highlighting primary thinking patterns and explanations of features in the IR spectra for each participant. Common codes were grouped together until only two groups remained. The titles of these groups will be referred to as themes throughout the rest of this chapter. A test of inter-rater reliability of 20% of the data initially yielded 67% agreement. Upon further discussion and analysis, the raters were able to come to 100% coding agreement. The conceptual sophistication of student responses were also determined using the framework of the *Chemical Thinking Learning Progression* (CTLP).[32] A more detailed explanation of the CTLP framework, including an explanation of conceptual sophistication and an assumptions-based approach to analysis, can be found in Chapter 3. The same terminology (e.g., intuitive, mixed, normative) will be used in this chapter.

Quantitative Analysis. Raw data (e.g., gaze position) were transformed to fixation data by Tobii Studio 3.2.3 software. Based on previous eye tracking studies in chemistry education research, a fixation threshold of 100 ms was used.[50,51] AOIs were defined for the following features of the visual stimulus:

1. The question.

2. The structural representations of the molecules. Two AOIs were defined for Compound 2 – one for the trichloromethyl group and one for the methyl group.
3. Each horizontal and vertical axis.
4. Each peak in the IR spectra.
5. Each baseline section of the IR spectra, defined as the region between peaks.

The colored regions in Figure 4-2 show the defined AOIs. The use of AOIs within the software allowed for the aggregation of data based on researcher-defined features. Within the bounds of each AOI, fixations were analyzed for frequency and duration.



Here are the same molecules with their corresponding infrared spectra.
Explain how each molecular structure causes the peaks in the spectrum below it.

Figure 4-2. Researcher-defined AOIs for the question (green), molecular structures (yellow), IR spectra axes (blue), IR peaks (red), and IR baselines (grey).

For each participant, the following data were exported from the software based on the raw eye gaze input (i.e., gaze point, validity code; see *Eye Tracking System*, above) and the researcher-defined AOIs:

- Fixation count (FC): Number of distinct fixations within each AOI
- Fixation duration (FD): The length of time (ms) of a fixation

Because the length of time each participant viewed the stimulus varied, the durational data were divided by the total fixation duration of all fixations within every AOI to give a percentage of total fixation time in each AOI for each participant. This method has been previously established in the literature.[49]

In addition to fixation duration and count, eye gaze sequences were analyzed using *eyePatterns*, an open source software tool.[91] To use *eyePatterns* it is necessary for the gaze pattern data to be a string of characters with each character representing a particular AOI. Because Tobii Studio does not support the export of sequence data, the raw data were exported from the software and Microsoft Excel was used to translate AOI fixation sequences to a string of characters. Figure 4-3 shows the characters that were assigned to each of the 21 AOIs.

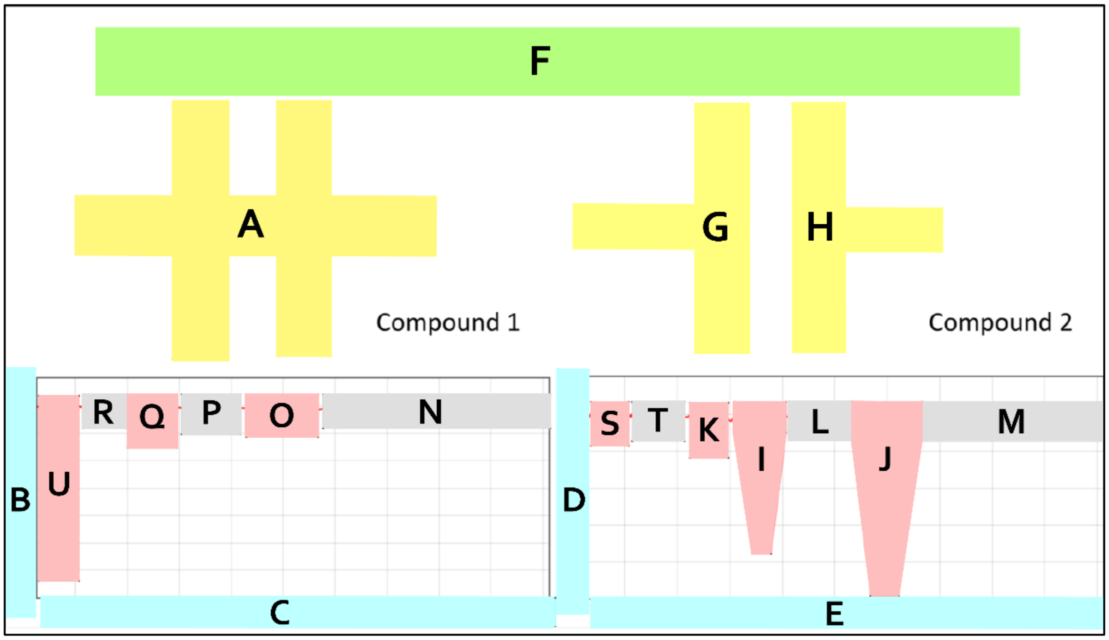


Figure 4-3. AOIs were assigned letters A through U for the purpose of sequence analysis.

After obtaining a character string for each participant, the data were exported to *eyePatterns* and the "Pattern Finding" tool was used to identify fixation patterns of the collapsed sequence. In a collapsed sequence, a participant's multiple successive fixations within a single AOI were collapsed into a single gaze or dwell for the purposes of sequence analysis. For example, the sequence AAAAAGGHHHH would be collapsed to AGH. This decision is based on prior practice found in the literature.[91] The pattern finding tool is used to provide the frequency for each possible transition in lengths greater than or equal to two characters. For this analysis, 3-character fixation sequences were chosen based on suggestions from the literature that this is the maximum sequence that can be interpreted.[92,93] Analysis was simplified by looking only at the top occurring sequences.

Results and Discussion

Qualitative Analysis

The qualitative coding resulted in the emergence of two primary themes: ATOMS and BONDS. Participant explanations based on an ATOMS approach focused on the identity of the molecular components and related differences in the IR spectra as being the result of differences in the presence or absence of certain elements. Participant explanations based on a BONDS approach focused on the connections between components of the molecule and related differences in the IR spectra as being the result of differences in the arrangements of molecular components. Later in this chapter, each of these themes will be referred to as a *thematic focus*. Figure 4-4 shows the percentage of participants within each educational level who demonstrated either an ATOMS focus or a BONDS focus. As indicated in the figure, students at increasing educational levels has fewer atoms-focused explanations and more bonds-focused explanations. Further examination of the data in each theme revealed additional insights.

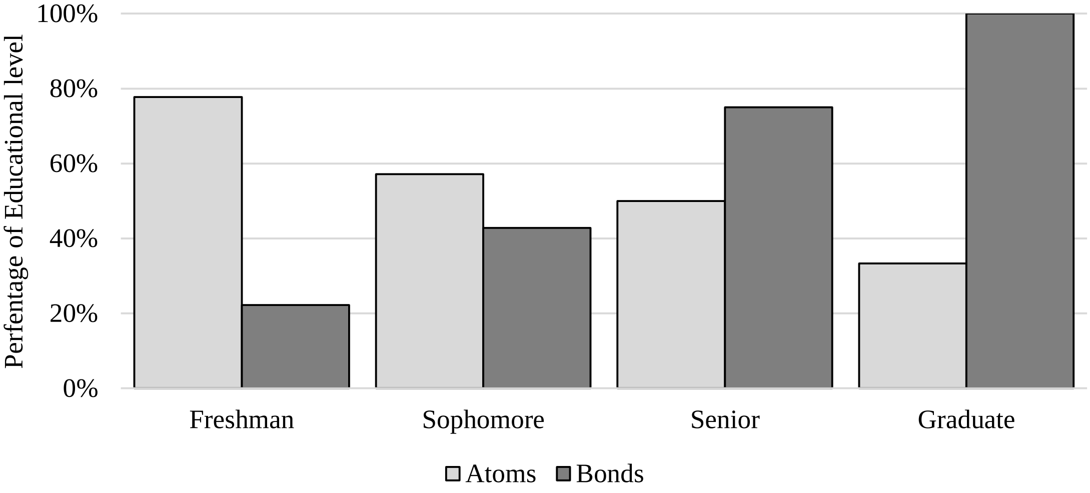


Figure 4-4. Percentage of participants at each educational level who focused on ATOMS or BONDS when answering the question.

Thematic Focus on Atoms. Assumptions based on components of the molecules appeared in 58% (n=15) of participants when reasoning about the provided spectral features. These explanations varied in the way in which they were used, with students talking about atoms by quantity, type, molecular weight, energy absorption, and vibration. Atoms-focused explanations ranged in sophistication from intuitive to hybrid and were most prominent among freshman participants. For example, one freshman explained the differences in the spectra based on the differences she was able to observe in the molecules:

> ***F7:**... I think that's because it* [compound one] *has hydrogen and carbon and the second one, compound two, has three different compounds, three compound, yeah, three different elements. It has hydrogen, carbon, and this Cl. So that causes the difference in the peak.*

This student explained a phenomenon that was new to her (i.e., IR spectroscopy) using explicit cues from the molecular structures, namely elemental composition. Another freshman student made a similar remark when she talked about the molecules and their spectra, but instead of focusing on the differences between the molecules, she focused on how the spectra were representative of their respective molecules:

> ***F5:** I think each atom has like a certain place where it gets absorbed and that's, that's where... how each molecular structure causes the peaks...each atom gets transmitted, each atom gets, like, shown for each peak.*

Again, this student focused on explicit cues of the molecular structure in order to explain a phenomenon that she does not seem to fully understand.

Moving to higher level of conceptual sophistication, a sophomore demonstrated a hybrid level of conceptual sophistication when he indicated he knew IR spectra were the result of vibrations, but did not speak about these vibrations in relevant terms. Instead, he discussed the elemental composition of the provided compounds:

> **S5:** *The peaks in the spectra of compound two would have to be due to the difference in the amount of chlorine atoms in compound two relative to compound one. Um, because if the chlorine atoms were, um, taken out and hydrogen was thrown in, it would have an identical spectrum, but because there are three different atoms around one of the carbons it's going to have a different spectra because the spectra is, like, a fingerprint to the molecule.*[…] *The vibrations that the chlorines exhibit in spectrum two, I would assume would be at that fourteen, uh, micrometer wavelength because that's the difference between the molecules is the three chlorines around the carbon from compound two to compound one.*

S5 is bringing his academic knowledge (i.e., IR spectroscopy detects vibrations) to bear on a novel scenario, but his application of the knowledge is incorrect, specifically he seems to think the vibrations occur in the atoms instead of the bonds.

Another sophomore student invoked knowledge of IR spectra from class, stating that it was about functional groups, but again was relying on the atoms to explain the peaks. She also became confused when two of her reasoning paths seemed to conflict:

> **S7:** *IR is functional groups. There's nothing with... there's carbon-carbon, carbon-hydrogen, but there's no carbon-chlorine functional group…There's only two peaks but there's three chlorines, so... Can I say I don't know?* [long pause]

> *Um... there's three chlorines but there's only two large peaks. There's one peak difference with the…ethane but, that's because that same peak doesn't appear so that peak relates to the second carbon. I don't know. So, there's one common peak between the two, which is probably going to be the carbon-hydrogen, and then there's something else that's slightly similar at twelve micrometers, but the two peaks... the two peaks must be from the…chlorine…even though that's not a functional group.*

S7's chemistry knowledge, combined with her own intuitive ideas, provided her with conflicting ideas, as evidenced by this train of thought: (1) IR peaks show functional groups; (2) the differences in the peaks must be because of the differences in the molecular structures; (3) the presence of chlorine in Compound 2 is the only difference between the compounds, therefore it must be causing the peaks that are different; and (4) chlorine is not a functional group, therefore it should not show up on an IR spectrum. In the end, she reconciles them when she says, "even though that's not a functional group" – a recognition that something in her knowledge bank must be incorrect.

Not all students based their explanations on explicit cues. For example, a freshman student based her response on molecular weight, an implicit cue:

> **F2:** *The chlorine causes more peaks…maybe because it has a higher molecular weight than the other one?*

While F2 cued on the differences in composition and reasoned that these caused the difference in spectra, she chose an explanation based on an explicit cue. While the cue is appropriate, the use of knowledge in her response is intuitive in nature. Hence, the reasoning is considered to be hybrid - a mixture of intuitive thinking and analytical reasoning based on scientifically accepted models

Thematic Focus on Bonds. Assumptions that bonds and bonding were responsible for the observed properties were noted in 54% of participants (n=14) when explaining the relationship between molecular structures and their associated spectra. As with the ATOMS approach, participants' usage of the BONDS approach relied on a number of cues, including the number and types of bonds, length and angle of bonds, types of vibrations, and distributions of electron density. Student responses that focus on bonds ranged from intuitive to normative in conceptual sophistication and primarily appeared among seniors and graduate students.

Only 22% of freshman-level students (n=2) focused on bonds when trying to explain the relationship between molecular structure and IR spectrum, but these explanations were limited in scope. For example, one of the students related IR spectra to the energies associated with breaking specified bonds:

> **F6:** *I'm assuming the difference* [between the spectra] *is because of the energies it takes to break up the connections between the different compounds. All the hydrogens would come off at the same time, although the chlorine would come off at a different point.*

F6 focuses on the connections between the atoms, or the bonds, as being responsible for the differences in the spectra. It is likely that this response is a direct reflection of topics being covered in F6's general chemistry course at the time of her participation in this study.

Most students focusing their responses on bonds and bonding demonstrated a better understanding of molecular properties (i.e., electron distribution models that depend on structural features of a molecule), but not necessarily the properties responsible for interaction with IR radiation. A good example of this situation comes from a graduate student:

> **GS5:** *So... the chlorine bonds, the polar nature of the bonds is... causing weaker interactions. So the lower energy to cause vibrational, um, motion, okay. I guess that's my answer.*

GS5’s response indicates that she has an understanding of IR spectroscopy (i.e., it has to do with vibrational motion) and bonding (i.e., the difference in electronegativity between carbon and chlorine is responsible for the bond being polar) but it is not clear if she understands the relationship between the two.

Some students who focused on bonds did so by identifying which bonds within the molecule were responsible for specific peaks in the spectrum. A sophomore-level student said:

> **S1:** *For compound number one, um, the peaks, I think, would be the carbon single bond and the carbon-carbon single bond, and the carbon-hydrogen single bonds, and for compound number two, um, the big peak would be the carbon-chlorine and the carbon-carbon single bonds again.*

It appears that S1 is giving the type of response she was trained to give in her organic chemistry course by simply identifying the peaks. While she may be relying on correctly memorized bond-peak associations, this response does not demonstrate that S1 understands why certain peaks are associated with specific structural features.

Participants in the uppermost educational levels displayed the most advanced chemistry knowledge in their responses, as indicated by their responses cuing on types of vibrational motion (i.e., stretching and bending), rotation, symmetry and dipole induction and energy absorption.

Of particular prevalence among seniors and graduate students was an indication that IR spectroscopy is related to the vibrational motion of the molecules, particularly bending and stretching. Most graduate students also connected these vibrational motions to energy absorption. GS4 provides a good example:

> **GS4:** *So you've got absorbance from ethane, which is just primarily due to carbon-hydrogen stretching and bending and then you have* [compound 2], *which has more peaks corresponding to different groups from the chlorine so you can get a chlorine stretching, bending, so it has other wavelengths associated with those other energies that it can absorb at, as opposed to just carbon-hydrogen stretching and bending.*

Even more specific than that, graduate students also allude to an explicit requirement of IR spectroscopy: the vibrational motion must alter a dipole in order to be detected. GS3 was one such student:

> **GS3:** *…vibrations, because that's what infrared detects is vibrational modes of your compounds. Hm. Well, vibrational modes, obviously, yes, but you have to induce a dipole.*

Findings from the qualitative analysis of think-aloud transcripts tell a story that is apparent to all chemistry educators and education researchers: with higher content knowledge comes an ability to better understand and interpret visualizations of molecular structures and IR spectra. However, the findings presented above also add to the story: students have to shift from a focus on atoms to a focus on bonds in order for knowledge to be integrated properly.

While inspection of think-aloud transcripts provided useful information for identifying assumptions about structure-property relationships, the protocol used did not allow for the interviewer to ask follow-up questions to gather additional cognitive information from participants. Therefore, an analysis of the quantitative eye tracking metrics was undertaken to further uncover possible underlying assumptions.

Quantitative Analysis

Analysis of quantitative measures was used to determine participants' eye gaze behaviors and patterns with the intent to provide a complete picture of students' reasoning about structure-property relationships. With a larger participant pool, it would be appropriate to analyze the data via an ANOVA or Student's *t*-test, both of which are used to compare means, albeit under different circumstances. Both of these parametric statistical tools have at their core an assumption of normality, however normality of the data was questionable because of the small sample sizes. Before beginning analyses of fixation count (FC) and fixation duration (FD) measures, a Shapiro-Wilk test was applied to each measure to test for normality. Each Shapiro-Wilk test resulted in $p < 0.05$, indicating that the data are not normally distributed. Therefore, for the remainder of this section, a descriptive approach is taken to present the quantitative data. Data plots are of averages only. A representation of uncertainty (i.e., error bars) has been purposefully excluded from the figures because it provides no useful additional information to the data set. For tables, both mean and median are shown to further illustrate that normality is not present among the data.

To simplify explanations, AOIs of similar type were aggregated for analysis. The resulting AOI groups were:

- *Molecules*: Any AOI containing, either partially or entirely, the structural representation of the compounds. AOIs A, G, and H were gathered into this grouping.
- *Baseline*: Any AOI containing a part of the spectra that was not considered a peak. AOIs R, P, N, T, L, and M were gathered into this grouping.
- *Peaks*: Any AOI containing on a spectral peak. AOIs U, Q, O, S, K, I, and J were gathered into this grouping.
- *Question*: The AOI (F) containing the question.
- *Axes*: Any AOI containing an x- or y-axis of the IR spectra. AOIs B, C, D, and E were gathered into this grouping.

Viewing Times. Viewing time is the total amount of time that a participant viewed the stimulus from the time it appeared on the screen until the time that the participant indicated he or she had finished answering the question. As a result, an examination of viewing times can serve to indicate how long it took the participant to provide an answer to the question. The mean viewing time across all participants was 166.8 s (SD = 140.7, Median=116.1). Table 4-2 shows the mean and median viewing times for participants within each educational level. In general, the higher educational levels had longer viewing times. This indicates that it took seniors and graduate students longer to answer the question. A review of think-aloud transcripts indicates this is because participants in these upper educational levels had more to say when answering the question. This may mean that greater depth and breadth of content knowledge allowed senior and graduate student participants to recognize and interpret more of the information represented in the visualizations of the stimulus.

Table 4-2. Stimulus viewing times by educational level.

	Mean (s)	**Standard Deviation**	**Median (s)**
Freshman	118.8	83.7	66.0
Sophomore	108.7	60.4	88.4
Senior	227.7	181.3	192.8
Graduate	226.2	200.2	197.8

Total Fixation Count. The number of fixations within an AOI, categorized by educational level and thematic focus, is provided in Table 4-3. To determine mean, standard deviation, and median, the number of fixations that occurred within any AOI were summed for each participant, giving the total fixation count (TFC). The descriptive statistics were calculated based on groupings by educational level and thematic focus.

Table 4-3. Total fixation counts by educational level.

	Mean	Standard Deviation	Median
Educational Level			
Freshman	159.0	83.8	131.0
Sophomore	203.4	123.2	159.0
Senior	326.0	324.1	218.0
Graduate	507.0	383.4	279.0
Thematic Focus			
Atoms	179.1	113.6	145.0
Bonds	350.4	324.3	250.0

In general, higher educational levels had a greater number of fixations within AOIs. Using the lens of the eye-mind assumption, it can be said that each fixation represents a connection between what the eye is viewing and the mind is processing.[69] Thus, the greater number of fixations by graduate students indicates they are processing more types of information available in the stimulus than participants at lower educational levels do. An alternative explanation is that a greater number of fixations indicates that a participant is doing more searching without processing what is viewed. However, it seems sensible to expect participants with less content knowledge (i.e., freshmen) to perform more searching, which is not supported by the evidence.

The TFC data also show that participants with a thematic focus on bonds had a greater number of fixations than participants with a thematic focus on atoms, which is consistent with data from the qualitative analysis, which indicated that the majority of atoms-focused participants were at the freshman-level and the majority of bonds-focused participants came from the senior and graduate student levels (Figure 4-4).

Percentage of Total Fixation Count (TFC). The percentage of TFC was determined by dividing a participant's fixation count for an AOI group by his or her total number of fixations for the stimulus. Thus, each participant had a percentage of fixations for each AOI group. The average percentage of fixations within each AOI group for each educational level is shown in Figure 4-5. The two AOI groups with the highest percentage of TFC were *Molecules* and *Question*. The high percentage of fixations within the *Question* AOI is not a surprising result, as the fixations are a result of participants reading the text. According to the eye-mind assumption,[69] the increased number of fixations within the *Molecules* group indicates that participants spent more time processing information in those AOIs. Given only this piece of information, though, it is hard to say whether the increased processing was because the information contained in the molecular structures took more time for participants to understand or if the additional fixation counts occurred for some other reason.

The data also show that freshman-level participants had more fixations on the question. Tang and Pienta[50] found similar results, noting that students who were unsuccessful at solving a gas law problem had a higher occurrence of fixations on the question.

Another notable finding is that senior and graduate student level participants had a higher percentage of TFC on the actual spectra (i.e., *Peaks* and *Baseline*) than participants from lower educational levels. This indicates that participants at lower educational levels saw less relevant information contained in the spectra, or that they were unable to interpret the information the spectra contained.

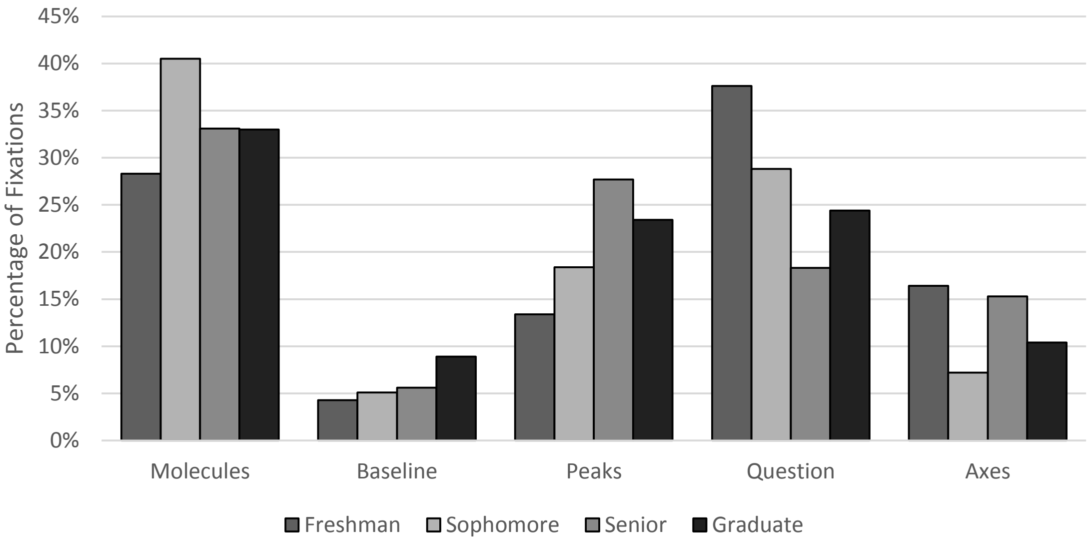


Figure 4-5. Percentage of fixations within each AOI group sorted by educational level.

Figure 4-6 shows the distribution of percentage of TFC sorted by thematic focus. These results show a trend that is similar to the distribution seen when grouping the data by educational level. This is likely due to the fact that the students using an atoms-focused approach to respond to the question were primarily freshmen. Findings from Figure 4-5 and Figure 4-6 are consistent with each other.

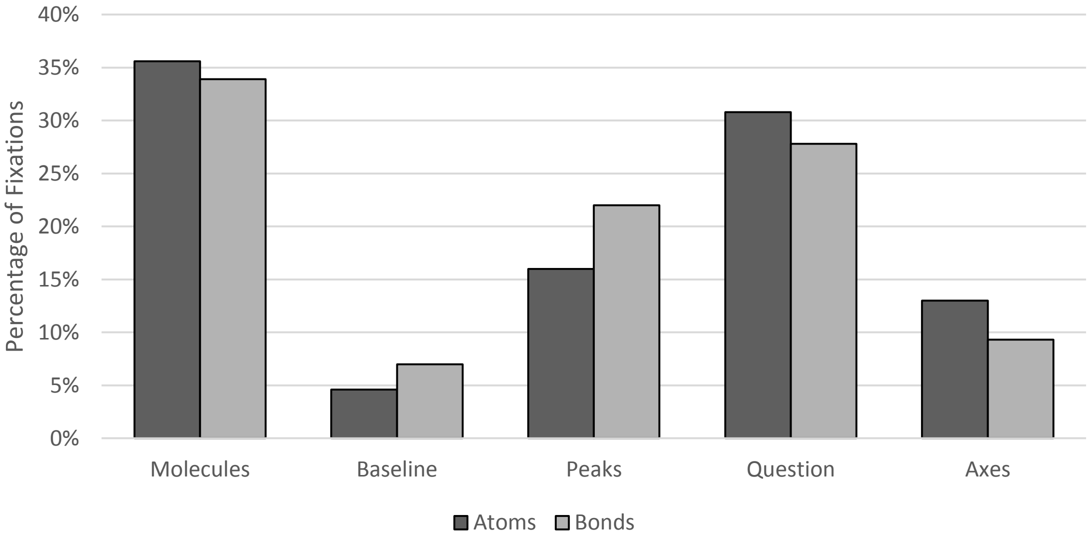


Figure 4-6. Percentage of fixations within each AOI group sorted by thematic code.

Total Fixation Duration. Fixation duration (FD) is the amount of time a participant's gaze is fixated within an AOI. Fixation durations for all AOIs were summed for each participant, giving a total fixation duration (TFD). In other words, this measure indicates how much time each participant group fixated on *any* of the AOIs within the stimulus. Summation of individual participant FD was used to determine the data shown in Table 4-4.

The TFD data show trends that are consistent with the TFC data above. In general, participants from higher educational levels spent more time fixating within AOIs. This finding could be an artifact of the viewing time data (i.e., more time spent viewing the whole stimulus inevitably leads to more time fixating on the AOIs) or indicative of the increased mindful processing of information contained in AOIs by students at higher educational levels.

Table 4-4. Total fixation duration, in *seconds*.

	Mean (s)	**Standard Deviation**	**Median (s)**
Educational Level			
Freshman	35.0	21.9	29.5
Sophomore	47.7	37.1	42.5
Senior	79.0	78.2	54.3
Graduate	142.5	127.9	59.6
Focus			
Atoms	40.2	33.0	30.0
Bonds	92.0	99.4	59.5

Percentage of Total Fixation Duration. For each participant, a percentage of TFD for each AOI group was determined by dividing the fixation duration, in seconds, for an AOI group by the TFD for all AOIs. Percentage of TFD was used because participants viewed the stimulus for different amounts of time, thus an examination of TFD alone would not be a valid means of comparison. These data were sorted by educational level and thematic focus and are shown in Figure 4-7 and Figure 4-8 respectively.

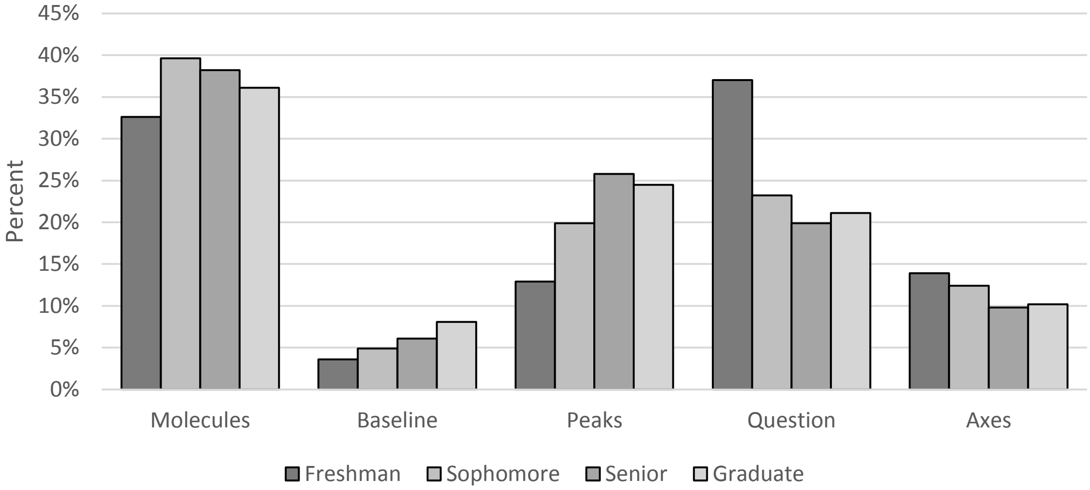


Figure 4-7. Percentage of total fixation duration for each AOI group sorted by educational level.

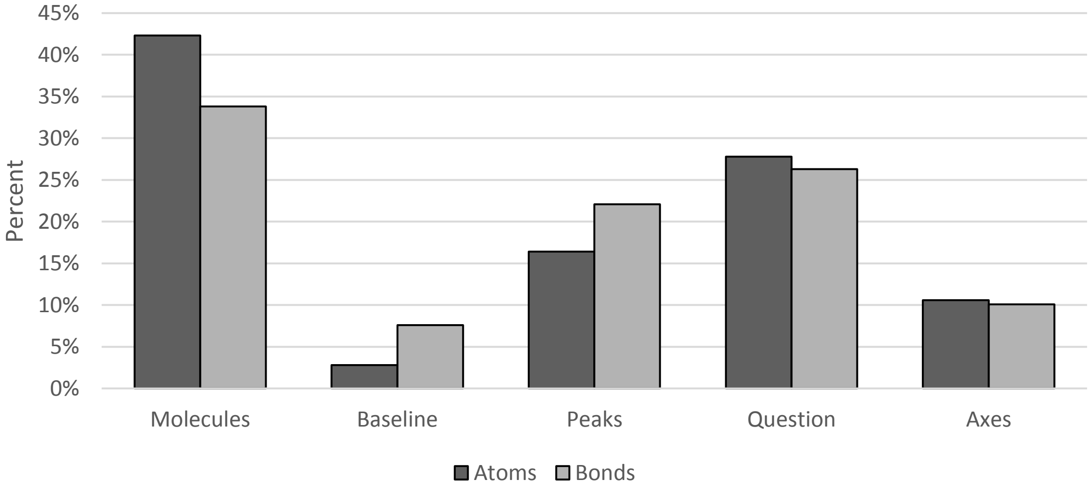


Figure 4-8. Percentage of total fixation duration for each AOI group sorted by thematic focus.

Percent TFD data are consistent with percent TFC data above. AOIs in the *Molecules* group were the most viewed, followed by the *Question* AOI. Participants at higher educational levels spent more time viewing AOIs highlighting parts of the spectra (i.e., *Peaks* and *Baseline*) than the freshman- and sophomore-level participants. Freshman-level participants spent more time than the other educational levels viewing the *Question*. Once again, the educational level and thematic focus groupings are consistent with each other, bearing in mind that most freshmen were in the atoms-focused group and most graduate students were in the bonds-focused group.

Individual Fixation Duration. For each participant, an average FD for individual fixations in each AOI group was determined. This will be referred to as individual fixation duration (IFD) to distinguish it from TFD described above. IFD data can provide more evidence to (1) determine processing time for each type of visualization in the stimulus and (2) infer whether or not participants are searching for meaning among the visualizations. These data were sorted by educational level and thematic focus and are shown in Figure 4-9 and Figure 4-10, respectively.

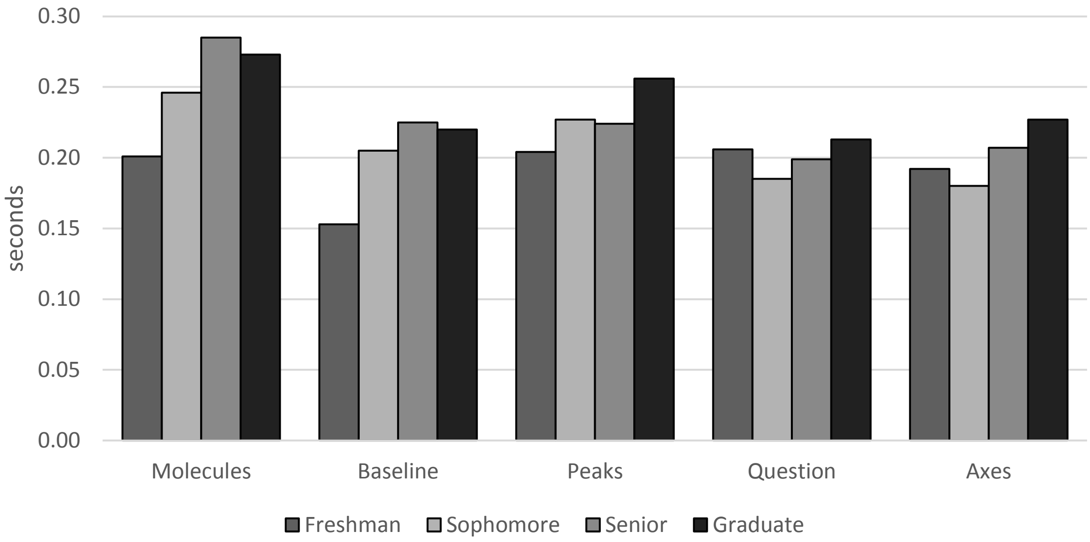


Figure 4-9. Average individual fixation duration for AOI groups by educational level. *Note: Only pauses in eye movements longer than 100 ms were counted as fixations.*

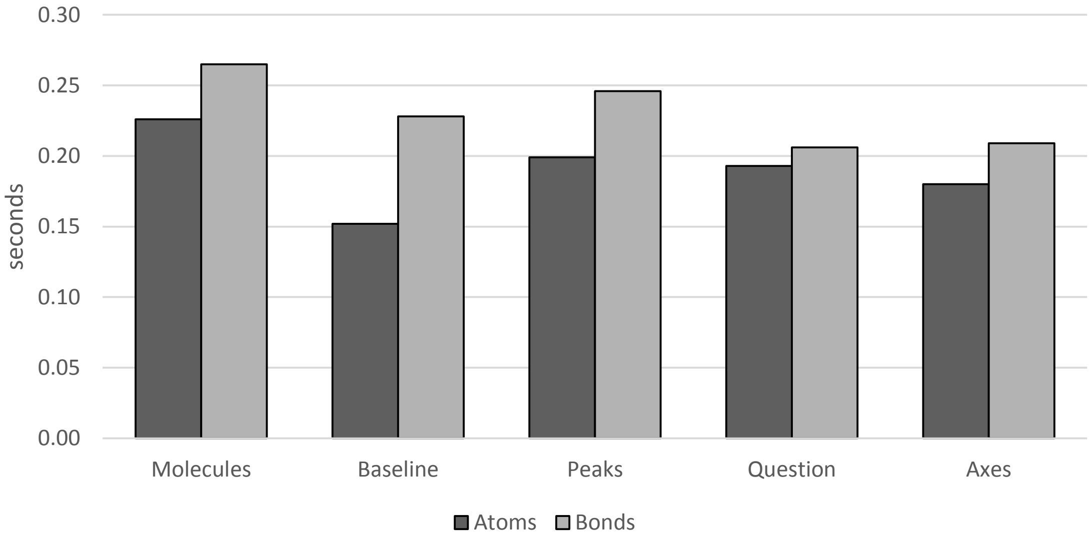


Figure 4-10. Average individual fixation duration for AOI groups by thematic focus. *Note: Only pauses in eye movements longer than 100 ms were counted as fixations.*

Freshman-level participants had shorter fixations than participants at other educational levels for the *Baseline* and *Peaks* AOI groups, which is consistent with percent TFC (Figure 4-5) and percent TFD (Figure 4-7) data. These same participants also had shorter fixations for the *Molecules* AOI group, in agreement with TFD data. However, freshmen show the highest percent TFC results for this same AOI group. This appears to indicate that the freshmen participants were searching within the molecular structures for relevant information that would help them answer the question, but likely disregarded information within the visualizations of the spectra. For the remaining educational levels, these findings appear to confirm that participants were not randomly searching to find meaning in the visualizations, as might be concluded from FC measures alone. This is further evidence that participants looked at visualizations that had meaning to them: the molecular structures for freshmen and the spectra for seniors and graduate students, with the sophomores being more evenly distributed among the AOI groups. As with findings drawn from all previous measures, educational level and thematic focus groupings are consistent with each other.

Sequence Analysis. Eye fixation sequences can reveal perceptual strategies that people develop for interpreting visual stimuli.[47,93,94] In order to understand the possible viewing strategies employed by participants, a sequence analysis was carried out to identify the number of occurrences for every possible three-character sequence, where each character, A through U, represents an AOI (see Figure 4-3). Because there are a large number of possible permutations of 3-character sequences, it made sense to look at the most frequently occurring sequences from each of the educational levels. The sequence patterns were labeled descriptively (i.e., "sequence AGH is comparing the structural features of the two molecules to each other") and grouped according to these descriptions. The resulting identified patterns, including their descriptions and examples, are given in Table 4-5.

Table 4-5. Patterns that resulted from an analysis of the five most frequently occurring sequences for each educational level. *Note: Refer to Figure 4-3 for AOI labels.*

Pattern	**Description**	**Examples**
1	Comparison of structural and compositional features	*AGH, GHG, AGA*
2	Return to the question	*AFA, FGH, FAG*
3	Comparison of structural features to spectral peaks	*HGI, JHG, JGH*
4	Determining the wavelength or transmittance of a spectral peak	*QCQ, IDJ*
5	Comparison of peaks only	*SKI, UIJ*

The occurrence of all sequences falling into the same pattern were summed and divided by the number of participants in the category to give a *Ratio of Occurrence* (RO). For example, the most frequently occurring sequences for freshmen were *AGA, GAG, GHG, HGH,* and *AFA*. Among these sequences, *AFA* is a Pattern 2 sequence, but the others are Pattern 1 sequences. The sum of the occurrences of the four Pattern 1 sequences is 42. There are nine freshmen participants. Thus the ratio of Pattern 1 occurrences to freshman-level participants is 4.67. In other words, the RO is the number of times that a viewing pattern appeared per participant on average.

To test the validity of using only the most frequently occurring sequences, the occurrences of all possible sequences for Pattern 1 were examined to find an RO for each educational level. These results are presented in Figure 4-11. The resulting RO values show a similar trend to that seen when looking at only the most frequently occurring sequences. This evidence supports the validity of only looking at the most frequently occurring sequences.

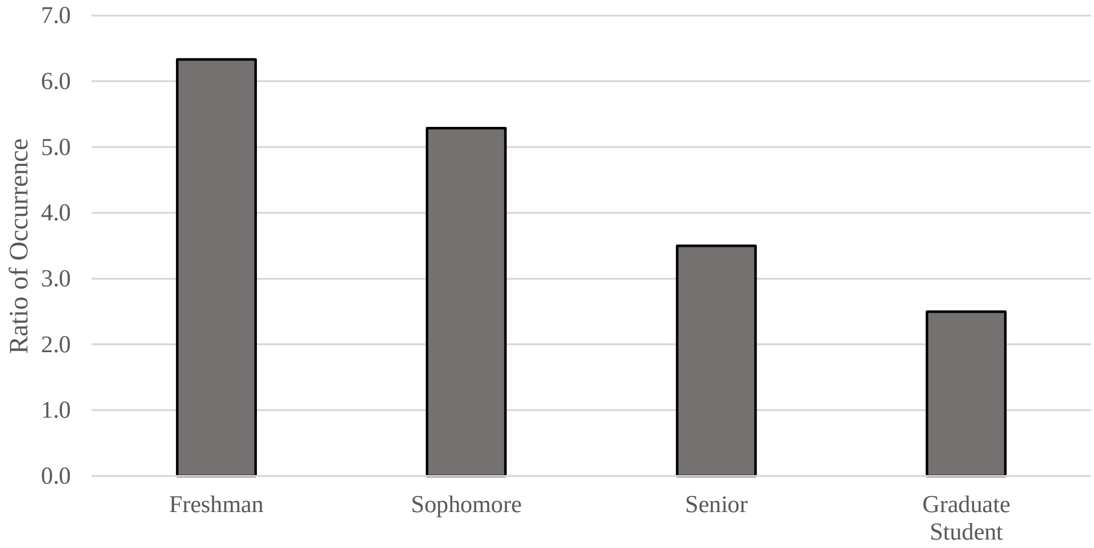


Figure 4-11. Ratio of occurrence for all Pattern 1 sequences by educational level. The ratio of occurrence is the number of times that a viewing pattern appeared per participant on average.

The ROs of each viewing pattern by educational level and thematic focus are shown in Figure 4-12 and Figure 4-13, respectively. The RO of Pattern 1 sequences is highest at the freshman level and lowest at the graduate student level. Participants using this viewing pattern more frequently appear to be comparing the structural and compositional features of the two molecules in order to identify differences that would allow them to answer the question. This conjecture is further supported by examining the RO of Pattern 1 among atoms-focused participants. Sequences of the Pattern 1-type were the only ones among the top five occurring sequences for the group. Thus, participants whose responses focused on compositional features had viewing sequences that indicate they were focusing mostly on the molecular structures. Comparing freshmen to sophomores, the occurrence of Pattern 3 emerges. Pattern 3, a comparison of structural features to peaks, indicates the participant (1) understands that IR spectra are related to molecular structure and (2) is trying to relate specific peaks to specific structural peaks. Among sophomores, the primary comparisons of this type occurred for the two large peaks of the spectrum of Compound 2 (AOIs I and J, Figure 4-3), indicating that the participants are making an assumption that molecular differences show up only as large peaks in the spectra. Sequence data from seniors point to these participants' knowledge that spectral peaks can provide important information, no matter what their size. This is evidenced in the appearance of Pattern 5, which showed up only as the sequence S-K-I, where the AOIs S, K and I are for three peaks in the spectrum of Compound 2 (see Figure 4-3). This sequence indicates that participants recognized that important information can be found in comparing the peaks – perhaps by magnitude. Graduate students did not exhibit Pattern 5 in their most frequently occurring sequences. This is likely because they were using a different viewing pattern to interpret spectral information. This is demonstrated by the presence of Pattern 4 in their top-occurring sequences – a pattern that was not present in seniors' top-occurring sequences. Pattern 4 is a sequence that includes a spectral peak and a horizontal axis. Such a sequence indicates that a participant is trying to identify the wavelength of the peak, possibly to determine which structural feature results in the particular peak.

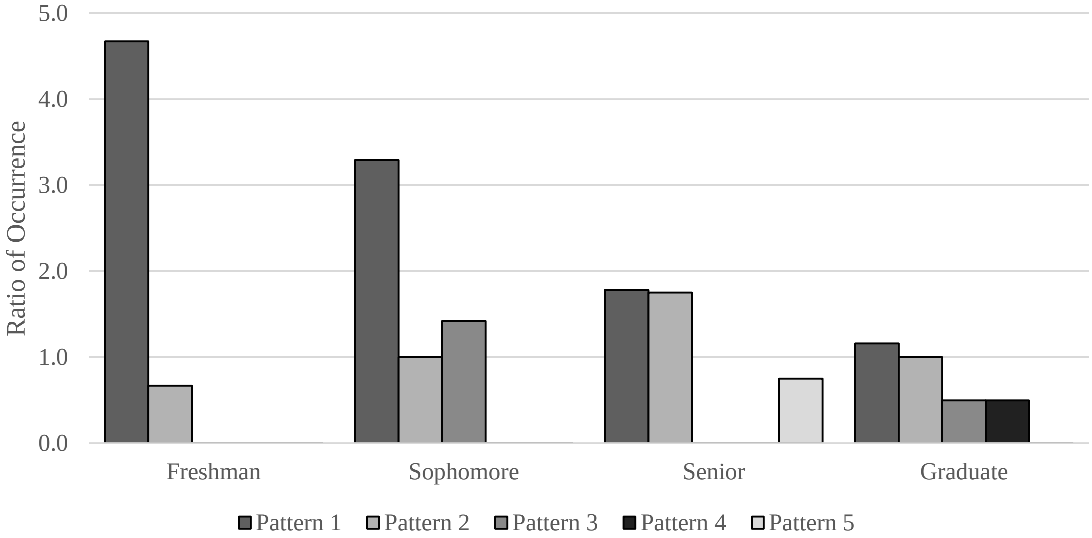


Figure 4-12. Ratio of occurrence of the five most frequently occurring sequences for each educational level. The ratio of occurrence is the number of times that a viewing pattern appeared per participant on average within each educational level.

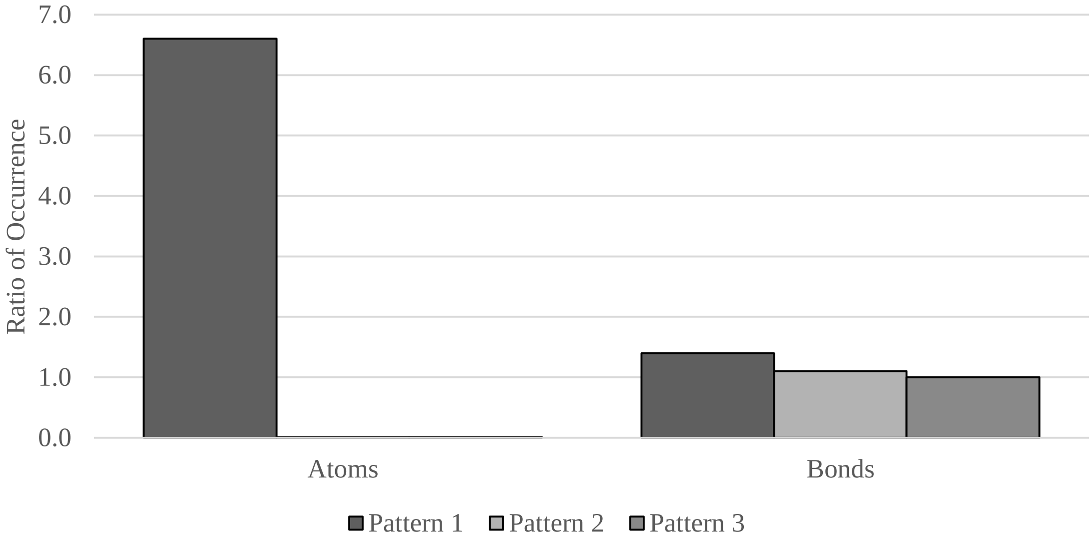


Figure 4-13. Ratio of occurrence of the five most frequently occurring sequences for each thematic focus. The ratio of occurrence is the number of times that a viewing pattern appeared per participant on average within each thematic focus grouping.

Only Pattern 1, Pattern 2, and Pattern 3 were represented among the five highest occurring sequences for the *Atoms* and *Bonds* groups. As mentioned previously, atoms-focused participants only had Pattern 1 sequences, which demonstrate comparisons of molecular features, among their five most frequently occurring sequences. Bonds-focused participants additionally showed occurrences of Pattern 2 and Pattern 3, indicating a more diverse viewing strategy in order to answer the question. For example, other than revisiting the question (Pattern 2), bonds-focused participants were also making comparisons between the molecular structure and the prominent peaks of the IR spectra (Pattern 3). Atoms-focused participants also had this viewing pattern appear in their sequencing, but not with high frequency. Only one sequence of the Pattern 3 type (HGI) occurred among the top eight most frequently occurring sequences – it was ranked eighth most frequent occurrence and its RO was low (0.63) compared to the bonds-focused participants.

Summary and Synthesis

The goal of this study was to uncover the ways that understanding, interpretation, and assimilation of information in molecular structures and IR spectra vary for students at different levels in their chemistry education. Results from quantitative and qualitative analyses of responses can be summarized as follows:

- In responding to the question in the visual stimulus, participants either focused on atoms or bonds.
- Freshman-level participants demonstrated searching behavior among the molecular structures.
- Sophomores, seniors, and graduate students looked at things that were meaningful to them, as opposed to simply searching.

- What the participants found meaning in was different for participants in different educational levels and with different thematic codes.
- Students at higher educational levels spent more time processing visual information that was relevant for answering the question.
- Freshman and atoms-focused participants primarily had gaze sequences that compared the molecular structures of the two compounds.

Taken together, these findings provide perspective on how students derive information from molecular structures.

Heuristics are reasoning strategies used to make judgments and decisions under conditions of limited time or knowledge.[95] One reason decision-making (ORDM; see Chapter 3) is one of several very common heuristics relied upon by novice chemistry students who generally have less content knowledge.[96] Talanquer defines ORDM as (p. 1094):[96]

> *When applying this "one-reason decision making" heuristic, individuals tend to follow these basic steps: (a) search for cues one at a time to differentiate between options (e.g., weight or electronegativity of atoms involved), (b) compare values of the selected cue for each alternative (e.g., which atom is heavier or more electronegative), and (c) stop the search when a cue is found that can be used to make a choice between options. In general, the final decision is based on selecting the option with the higher cue value on the selected criterion (e.g., it has the heaviest atom).*

Apparent reliance on ORDM can help explain the result that participants at lower educational levels expended less effort to process information on how the structure relates to the properties, as evidenced by FD, FC, and gaze sequence data. Instead, these students stopped looking once they found information they felt would answer the question.

Students at higher educational levels, on the other hand, have not only acquired more content knowledge relevant to answering the question, but they also have had more experience with analytical reasoning. These students spent more time processing the spectra than students at lower educational levels, as evidenced by the FD and FC data of seniors and graduate students. Additionally, gaze sequence data show that seniors and graduate students already knew which peaks to associate to particular bonds. A focus on bonds, rather than atoms, was also evident in their think-aloud transcripts.

Conclusions

In general, it can tentatively be inferred from this exploratory study that students who hold an assumption that molecules are collections of objects (thematic focus on atoms) attached to each other tend to apply direct causality when reasoning about how properties derive from features of molecular structure. On the other hand, students who hold an assumption that bonds are not objects but manifestations of energy through its interaction with matter (thematic focus on bonds) tend to reason in an ontologically different manner. They recognize the emergent nature of properties of a substance. This transition has been conjectured as a 'threshold concept' by Talanquer,[97] i.e., a shift in thinking such that observations are interpreted differently as a result of the new perspective afforded.

This study shows eye tracking is capable of detecting specifically what molecular features students pay attention to in order to predict molecular properties. In particular, the combination of qualitative analysis of think-aloud interviews to determine that students were making meaning of what they viewed, and eye tracking to discern viewing sequences and behaviors, allowed for the determination of relationships between different assumptions made by students about causal relationships between molecular structure and properties that a substance exhibits.

Future Work

The exploratory study that was conducted has some limitations. As an exploratory study, it enrolled fewer participants than a full-scale study would, and therefore, normalcy was not obeyed by the data and only descriptive statistics could be used to draw conclusions. A more robust study would include more participants. Furthermore, the study enrolled students at a single university, and participants are likely to have had the same professors in their courses. Thus, it is possible that the data could be skewed by an idiosyncratic tendency that one of the professors might have in how IR is taught. A more robust study would include students from at least one other university or who had one other professor for each course.

Even with sample size issues, this study has demonstrated the utility of eye tracking for studying other questions about structure-properties relationships, such as how best to teach students to determine molecular structures by examining the influence of instructional methods on eye gaze behavior.

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CHAPTER 5

CONCLUSION

Just as chemistry has always been a journey rather than a conclusion, green chemistry is also based on the premise that continual improvement, discovery, and innovation is the path towards the perfect goal of environmentally benign.

-- Paul T. Anastas and John C. Warner[1] --

The “path towards the perfect goal of environmentally benign”, referenced by Anastas and Warner above, is not as straightforward as one might think. The “perfect goal” requires more than improving and discovering new methods. It also means that chemists must strive to predict the full ramifications of their decisions and how to weigh benefits, costs, and risks of their choices. They also need to have a firm understanding of foundational chemistry in order to make and evaluate decisions of their practice.

The findings presented in this dissertation represent efforts to advance the practice of a green chemistry philosophy by studying two discrete sub-disciplines of chemistry: atmospheric chemistry and chemistry education. Chapter 2 provides information about the atmospheric degradation of a third generation CFC-replacement compound. Chapters

3 and 4 examine how chemists develop an understanding of benefits-costs-risks decision making and structure-property relationships, respectively. It is hoped that the findings presented in this thesis may contribute valuable insight for decisions in industry and in the education of future chemists. In the remainder of this chapter, a summary of key findings will be provided along with a discussion of their utility.

OH-Initiated Oxidation of HFE-7100

HFEs are a third-generation replacement for CFCs, a class of compounds whose manufacture and use is being phased out by the Montreal Protocol. While HFEs have desirable thermochemical properties as refrigerants, the fate of their use remains unclear. Thus research on potential degradation pathways is of the utmost importance if scientists are to prevent a global disaster like stratospheric ozone depletion. While the scope of work presented in Chapter 2 of this dissertation is small, a sound foundation for continued work was successfully laid.

In Chapter 2, the theoretical OH-initiated oxidation pathway was presented based on current literature. The degradation products of HFE-7100 were unable to be determined, but a successful calibration with UMBAR demonstrates the possibility to continue the work. Additionally, it was confirmed that the reaction of OH+NO occurs at a rate faster than OH+HFE.

The utility of this work for decision making through a green chemistry lens was made evident. Society has an established history of acting on new innovations without fully understanding the repercussions of such a decision. If this trend is to change, understanding the full environmental impact of HFEs, including their oxidation products, is of the utmost importance.

Benefits-Costs-Risks (BCR) Analysis

Chemistry is about both understanding phenomena of the natural world and advancing technologies for the benefit of mankind. Introducing the green chemistry philosophy to the everyday practice of chemistry has added an environmental stewardship component to the standard pursuits of the science. It has been unclear, however, how chemists develop abilities to evaluate the ramifications of their practice. Better training for the next generation of chemists demands that they be explicitly taught to think through the consequences of their work. In this dissertation, such thinking is referred to as BCR analysis.

Based on the work presented in Chapter 3, it is apparent that a large fraction of college students complete their chemistry degrees, or undergraduate chemistry courses required by their major of study, without reaching normative levels of BCR reasoning in chemistry contexts. In particular, the results of this study suggest that there are two transitions that could be aided by deliberately planned learning activities that occur in a coherent manner across the undergraduate chemistry curriculum. First, the transition from intuitive toward more advanced reasoning requires a shift from reliance on recognizable surface features (e.g., familiarity) and affect heuristics (assignment of "goodness" or "badness") toward noticing relevant chemical characteristics (e.g., reactivity under different conditions) and processes (e.g., different reaction pathways). Second, the transition toward more normative reasoning demands recognition of limitations of model-based explanations, greater emphasis on data-driven decisions, and specification of trade-offs.

Armed with this knowledge, the next step is to take this proposed progression of learning and build course content – curricula and instructional materials – that support the transitions to more advanced BCR reasoning. This content will provide chemistry educators with appropriate resources to educate chemists on the proper consideration of the impacts of their decisions, thereby advancing the practice of green chemistry.

Structure-Property Relationships (SPR) Thinking

A fundamental concept of chemistry is an ability to predict macroscopic properties of molecules based on their respective microscopic structural representations. For green chemists, this concept is even more important. Predicting a substance's properties provides information to aid in assessing environmental harm. It also affords the ability to determine reactivity and byproducts of use. The difficulties that students face when learning the core chemistry concept of SPR have been well documented in the literature. The established research, however, lacks direct means to relate student thinking to student viewing patterns of molecular representations. The study presented in Chapter 4 addresses this shortcoming.

In Chapter 4, concurrent use of a think-aloud protocol and eye tracking technology provided qualitative and quantitative data to uncover the ways that understanding, interpretation, and assimilation of information in molecular structures and

IR spectra vary for students at different levels in their chemistry education. Findings of the study make evident the problem that lower-level (i.e., freshman and sophomore) chemistry students have with cueing on inappropriate features when answering questions about the spectroscopic properties of a substance. Most frequently, students at lower educational levels relied on one-reason decision making as evidenced by quantitative eye gaze data. Students at higher educational levels, on the other hand, spent more time processing relevant features of the molecules and relating them to the IR spectra, as evidenced by eye gaze data. Think-aloud transcripts provided additional data to support these claims.

Perhaps the most significant contribution to knowledge of this study was to show that a method of eye tracking is capable of detecting specifically what molecular features students pay attention to in order to predict molecular properties. In particular, the combination of qualitative analysis of think-aloud interviews to determine that students were making meaning of what they viewed, and eye tracking to discern viewing sequences and behaviors, allowed for the determination of relationships between different assumptions made by students about causal relationships between molecular structure and properties that a substance exhibits. Even with sample size issues, this study has demonstrated validity of the methodology for studying questions of greater interest, such as how best to teach students to determine molecular structures by examining the influence of instructional methods on eye gaze behavior.

Final Comments

This dissertation has taken three approaches to the advancement of green chemistry as a philosophy of practice. First, there must be much more work done to determine the impacts of producing and using substances. As environmental stewards, which the philosophy of green chemistry encourages chemists to be, it is critical that chemists are able to base the evaluation of consequences in using new alternatives on empirical evidence that grounds theoretical predictions. A study of the OH-initiated atmospheric oxidation represents only a single aspect of the knowledge base that will be required to improve decision making in chemistry.

Secondly, helping chemists to become environmental stewards means training them to evaluate the benefits, costs, and risks that are inherent in making decisions of their practice. The development of a learning progression to describe how this understanding is acquired by chemists-in-training will help to improve the training of future green chemists, thereby improving their practice.

Finally, the pinnacle of green chemistry practice requires the prevention of environmental hazards before they occur. Predicting properties and reactions of substances means recognizing and understanding how molecular features give rise to such properties. Empirical evidence grounds theoretical predictions, but chemists must also be able to make theoretical predictions to guide experimental study. Central to the practice of chemistry are the abilities to predict the properties of a substance based on molecular structure, and to infer structural information from measured properties. The method of eye tracking that was developed to study students' abilities to reason about structure-property relationships has the potential to open doors for advanced study of these abilities in students.

APPENDIX A

A CASE STUDY OF REFRIGERATION COMPOUNDS

The board room is in an uproar. Fourteen stories above the streets of Boston, a very intense discussion is being held among ten very stubborn Executive Board members regarding the future of their company. You, being the newest member of the Board, sit quietly at your seat absorbing the conversation.

“This is what’s best for the bottom line!” The man belonging to this voice does not seem very happy. His name is Seth Whitmore and he is the Chief Financial Officer of the recently-formed Cryotek Refrigeration Systems, Inc.

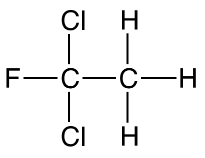
Catherine Green, the CEO, sits at the head of the table. She doesn’t look very happy either. “Yes we are all here to make money, but at what cost?”

The Executive Board is in the midst of a meeting to determine whether or not to renew the contract with the company's chemical provider. Cryotek currently uses a hydrochlorofluorocarbon (HCFC) in the air conditioners they manufacture. With the contract expiring, the company has a decision to make — stick to their current refrigeration compound or switch to something new.

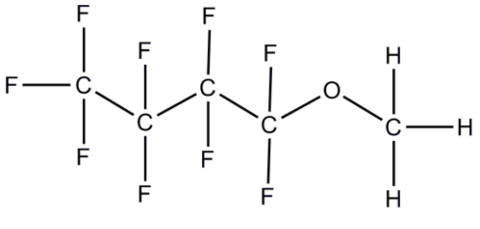
Catherine clears her throat before continuing. “I’d like our team of chemists to go over this one more time before the vote. Since they can’t come to a consensus, we’ll give each of them the opportunity to persuade us with their arguments.”

Edward Talbot, a balding man in a well-fitted white lab coat nods. “Certainly.” He rises to his feet and takes three steps to close the gap between his chair and the white board he will be using.

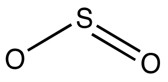
“I’d first like to remind you all what this discussion is about. The Cryotek 450R unit has been constructed. In its current configuration, we have the option of using three different refrigeration compounds. They are the hydrochlorofluorocarbon made by the company with whom our contract has expired, a hydrofluorinated ether, and sulfur dioxide.” He draws the chemical structures on the white board as he speaks, though some who are present in the room have to stretch their minds further than others to grasp the meaning imparted in a chemical structure.



HCFC 141b
hydrochlorofluorocarbon

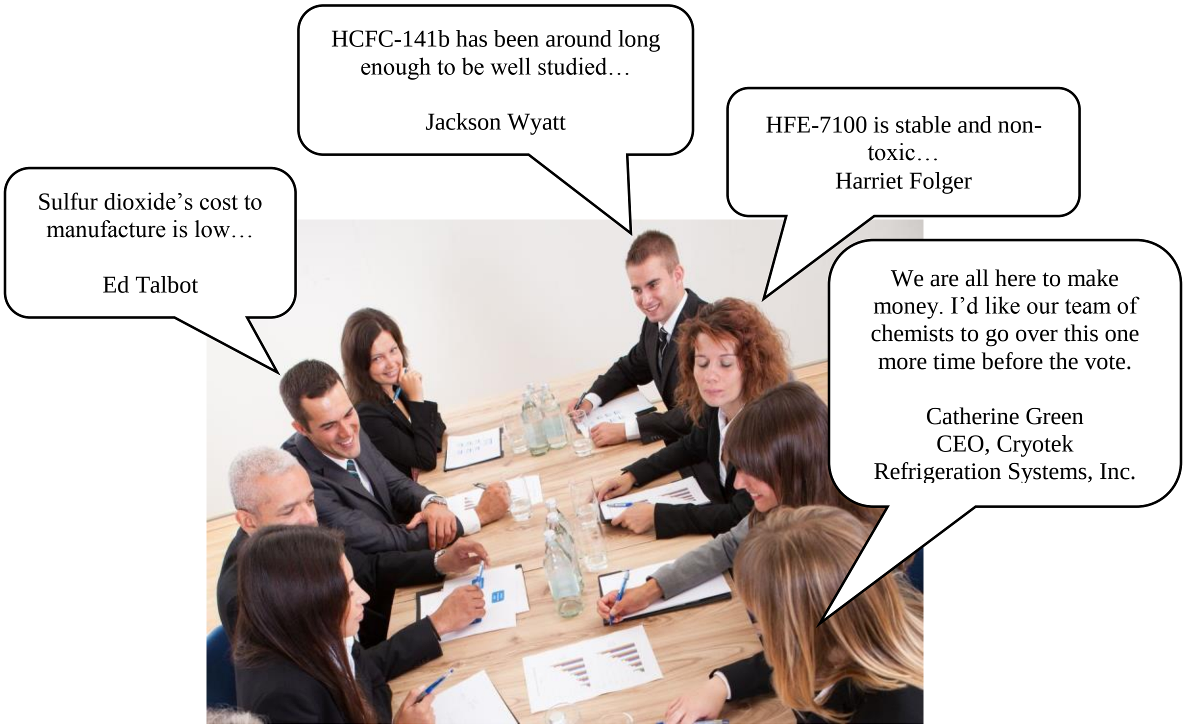


HFE-7100
hydrofluorinated ether



sulfur dioxide

Immediately, Seth points out the smallest of the molecules, SO_2. “That one is the cheapest to make, right? I think that makes it the best choice.” A couple of Board members mumble their agreement and nod their heads. Ed clears his throat and continues talking as if no one had interrupted. “It is my recommendation that sulfur dioxide be chosen for this unit. Its cost to manufacture is low and it still performs well during product testing.”



Andriy Popov/123rf.com

“What about the drawbacks?” The woman next to Ed Talbot places her palms on the table and rises to her feet next. Her name is Harriet Folger. “Sulfur dioxide is a toxic gas. A couple of whiffs of this stuff and our customers will be sick, or worse, dead. Not only that, but SO_2 is a poor decision for the environment. It’s a primary component of smog and can cause acid rain.” She shakes her head and begins pacing back and forth behind several of the board members. “No, the clear choice is this hydrofluorinated ether,” she taps the white board beneath the middle compound. “HFE-7100. It is stable and non-toxic, just a mild irritant if inhaled. It does not destroy the ozone layer and contributes very little to global warming. Yes, its cost to manufacture is higher than SO_2, but in the long run our customers will be much more satisfied.”

The man directly to the right of Harriet clears his throat. “I’m sorry, Harriet, but I have to disagree with your decision.” Jackson Wyatt does not bother standing up. His voice easily draws the attention of everyone at the table. He leans forward in his seat and slowly looks around at each of the Board members. “What Harriet hasn’t told you is that HFE-7100 isn’t well studied. Sure, we know it doesn’t deplete ozone or cause global warming, but we have no idea what happens to it when it gets released into the atmosphere. For all we know, it could break down into compounds that are much more harmful to the environment, or to people!” Now he was leaning back in his chair. “No, we should be using a hydrochlorofluorocarbon like HCFC-141b. It is every bit as stable and non-toxic as HFE-7100. The cost to manufacture is lower than HFE-7100 and it has been around long enough to be well studied.”

Ed shudders with laughter. “Pffft, your hydrochlorofluorocarbon is well studied all right, Jackson. Studied enough to know that those chlorine atoms are fully capable of destroying ozone if they get to the stratosphere. Not to mention that the global warming potential is higher than sulfur dioxide’s.”

Catherine takes command of the room then, as only a CEO could. “Thank you for that final word of input. We are now going to vote.” She passes 10 slips of paper around the table to the Board members, waits for everyone to write down their choices, and then collects the slips. As she finishes counting them, she looks up with mild surprise. “There are only nine slips of paper here and we’re looking at a three-way tie. Who didn’t vote?”

You shrink back in your chair. The absent voter was you. And now it seems that the future of this company lies in your hands.

APPENDIX B

GOKART INTERVIEW PROTOCOL

GoKart

Six Flags Amusement Park has asked you to design a GoKart (a small vehicle with an engine that kids can ride in). During your design phase, you must decide which fuel will power the GoKart. You are considering four fuels. First is gasoline, also known as octane, derived from petroleum. Second is also gasoline, but derived instead from wood pellets. Third, is natural gas, also known as methane. Finally, there is E85, which is mostly ethanol.

Jenny Zhang/123rf.com

If the fuels all cost the same per gallon, which fuel would you choose to power the GoKart? Why? Please say what your reasons are and what you think is important.

Which fuel would be best? Chemical names are in parentheses.

- Gasoline from petroleum (octane)
- Gasoline from wood pellets (octane)
- Natural gas (methane)
- E85 (ethanol)

How the fuels are available

It turns out that these fuels are available in different forms. Gasoline from petroleum and from wood pellets is available as a liquid. Natural gas is available as a gas. And E85 is available as a liquid.

Gasoline from petroleum (octane)	Gasoline from wood pellets (octane)	Natural gas (methane)	E85 (ethanol)
Liquid	Liquid	Gas	Liquid

Do you think this information is important in making a decision about which fuel is best? Does this information help you in your decision? Does it change your decision? Please explain your reasoning.

What the fuels are made of

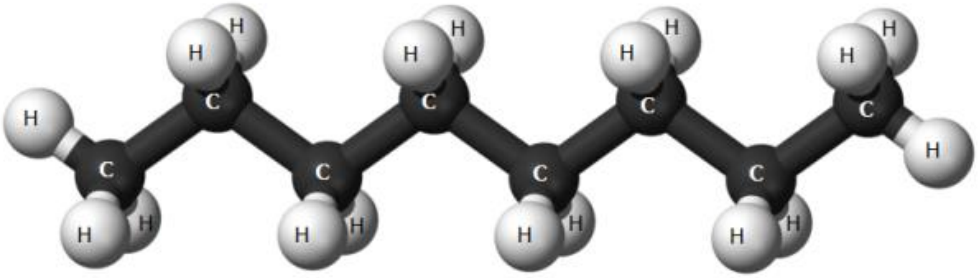
It turns out that we know what these fuels are made from. Gasoline from petroleum and from wood pellets is made of carbon and hydrogen. Natural gas is also made of carbon and hydrogen. E85 is made of carbon, hydrogen and oxygen.

Gasoline from petroleum (octane)	Gasoline from wood pellets (octane)	Natural gas (methane)	E85 (ethanol)
Carbon Hydrogen	Carbon Hydrogen	Carbon Hydrogen	Carbon Hydrogen Oxygen

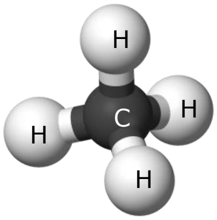
Do you think this information is important in making a decision about which fuel is best? Does this information help you in your decision? Does it change your decision? Please explain your reasoning.

Particles that make up the fuels

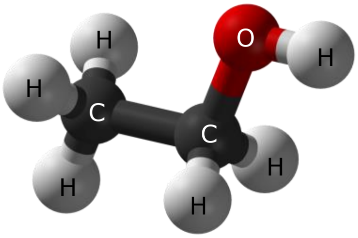
It turns out that we know about how the particles are arranged in the fuels. Here are drawings of how the particles are connected.



Octane



Methane



Ethanol

Do you think this information is important in making a decision about which fuel is best? Does this information help you in your decision? Does it change your decision? Please explain your reasoning.

Pollution

When fuels are used in engines, they can cause pollution.

In terms of how these four fuels would affect the environment, which one of the fuels do you think would be better than the others to use? Please justify your answer and explain your reasoning.

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