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Atoms versus Bonds: How Students Look at Spectra

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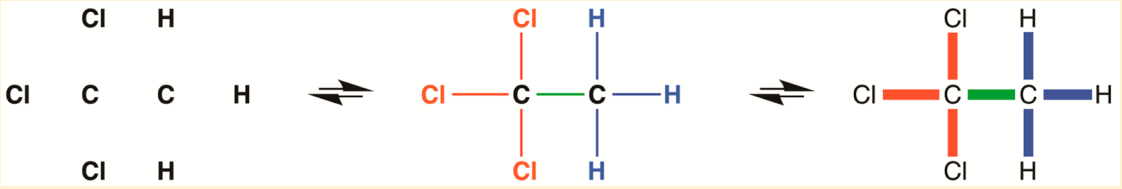

ABSTRACT: Students often face difficulties when presented with chemical structures and asked to relate them to properties of those substances. Learning to relate structures to properties, both in predicting properties based on chemical structures and interpreting properties to infer structure, is pivotal in students' education in chemistry. This troublesome but critical concept is often referred to as structure−property relationships. While there is no shortage of literature on students' difficulties with this concept, there is a lack of methodologies that can directly and quantitatively reveal underlying assumptions about structure−property relationships that constrain students' thinking. This study applied a "chemical thinking" lens to elucidate assumptions about structure−property relationships thinking. A combination of qualitative analysis using a think-aloud interview protocol was used with quantitative analysis of eye tracking data to probe students' reasoning when relating molecular structures of volatile hydrochlorocarbons to infrared spectral properties. Our initial findings offer partial validation of a newly developed methodology for analyzing eye tracking data to expose reasoning patterns that appear to correspond to identifiable underlying assumptions.

KEYWORDS: *First-Year Undergraduate/General, Second-Year Undergraduate, Upper-Division Undergraduate, Graduate Education/Research, Chemical Education Research, Spectroscopy*

FEATURE: Chemical Education Research

INTRODUCTION

A fundamental skill in chemistry is to predict macroscopic properties of substances based on their respective submicroscopic chemical structure representations. Spectroscopy is a ubiquitous tool for inferring molecular structure. The American Chemical Society Guidelines[1] that govern accreditation of undergraduate chemistry programs in the U.S. specifically emphasize its use. In addition to NMR, the Guidelines require that four of five categories of instruments be on site and used by undergraduates, where optical molecular spectroscopy is one of the five categories. Many researchers have stated the importance of learning to predict properties of substances based on their representations, be it macroscopic, submicroscopic, or symbolic.[2−6] Cooper and collaborators have studied how students make use of a variety of ideas to predict properties, such as melting and boiling points, based on molecular structures.[3,4] Sevian and Talanquer define *structure−property relationships* (SPR) as a crosscutting disciplinary concept of Chemical Thinking that is relevant to all aspects of practicing chemistry.[7] This crosscutting disciplinary concept is related to an essential question that chemistry allows us to answer: What properties does a substance have?

Despite the importance placed on this disciplinary idea, SPR is a challenging concept to grasp for students at all levels.[8,9] Difficulties students encounter with SPR have been the subject of a vast amount of literature in chemistry education. The most common problems among students seem to be the following:

(a) A reliance on heuristics to reduce the number of factors to be considered when reasoning about SPR.[3,10−14]
(b) 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.[13,15]
(c) 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).[13,16−18] Talanquer refers to this as inheritance thinking.[13]
(d) A general inability to reason about substances and processes at multiple spatial scales simultaneously.[3,5,8,19−21]

Researchers have studied a variety of properties that relate to chemical structures, including physical properties such as melting point and hardness,[3,4] and chemical properties such as reactivity.[22] Progress in reasoning about substance properties in relation to molecular structures, as training in chemistry increases, has also been studied. Cooper, Underwood, and Hilley[4] showed that, with increasing content knowledge, students increasingly reason about implicit characteristics of chemical entities in relating structure to properties. Bhattachar-

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yya[23] found that chemistry experts demonstrated commonality in three areas when using mechanistic reasoning about reactivity of substances: relating stepwise redistribution of electrons during a chemical process, having a broad body of knowledge of chemical reactions, and formulating working hypotheses to rationalize chemical processes as well as explain and predict them. We recently showed that less sophisticated thinking about SPR, in the context of evaluating fuel choices, is typically characterized by associations between features that are explicitly noticeable in molecular structures, while more sophisticated SPR thinking tends to cue on more implicit features of structures.[24] Taken together, these studies suggest that increasing conceptual sophistication in SPR thinking is characterized by a shift from (a) simple associations between explicitly noticeable structural features and observable properties toward (b) considering the validity of various hypothesized mechanisms that could account for how implicit features of structures are related to observable properties of those substances.

Chemical structures are communicated through representations. While there is a vast literature on the interpretation of representations,[25,26] and there is no shortage of literature on students' understandings and misconceptions of how they *think* about SPR, as noted above, quantitative measures directly relating these understandings and misconceptions to viewing behaviors of chemical structures is difficult to obtain. This study addresses a new question of how students' implicit assumptions constrain the ways in which they relate features of chemical structure representations to interpreting spectral properties. We explored the use of eye-tracking technology for this purpose, and present a new approach to studying students' reasoning in SPR problem solving.

Chemical Thinking as a Lens

In the Chemical Thinking framework, Sevian and Talanquer identify 11 core questions asked by chemists in their practice. These questions serve as variables along which the development of students' chemical thinking can be expected to progress (i.e., progress variables).[7] Any problem encountered by a chemist necessitates the use of one or more crosscutting disciplinary concepts (e.g., SPR) to answer relevant specific questions addressing the problem. Thus, each crosscutting disciplinary concept can run through any of the progress variables, and depends upon the problem being solved. For example, a chemist or a chemistry student could be faced with a problem of determining which biofuel would be best to use for a lawnmower engine. Part of this work may include determining what is in different biofuels (crosscutting concept of *chemical identity* in the progress variable, "What cues are used to differentiate matter types?"), doing experiments to figure out how much energy and what byproducts are produced under the conditions of the lawnmower engine operation (crosscutting concept of *chemical causality* in the progress variables, "What determines the outcomes of chemical changes?" and "What affects chemical changes?"), and making an evaluation of which biofuel is best based on a balance between different consequences, such as the toxicity of different byproducts and the energy efficiency of the biofuels (crosscutting concept of *benefits-costs-risks* in the progress variable, "What are the effects of using and producing different matter types?").

Relating chemical structures to spectroscopic properties is an activity that is often part of problems that involve identifying what substances are in a sample or what types of reactions could or did occur in a synthesis. Such activity involves the SPR crosscutting concept in one of the three progress variables shown in Figure 1. If a chemist is analyzing spectroscopic data, this problem requires an answer to the question, "How do properties of matter types emerge?"

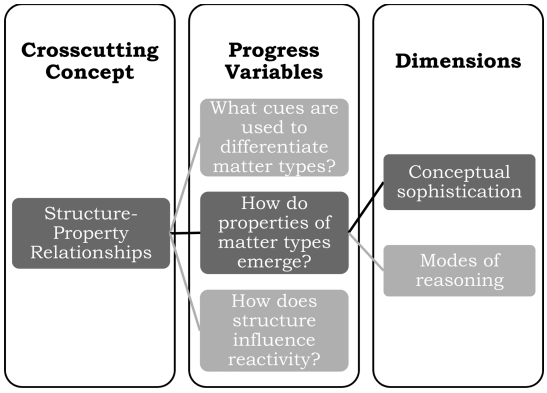

Figure 1. Illustration of relationships between constructs of the Chemical Thinking framework, showing the combination addressed in this study: (1) structure−property relationships (SPR) is the crosscutting disciplinary concept, (2) "How do properties of matter types emerge?" is the progress variable, and (3) this paper presents an analysis of the conceptual sophistication dimension of this progress variable.

In the framework, each progress variable is measured along two dimensions: conceptual sophistication and modes of reasoning. For this study, we limited our analysis to the conceptual sophistication dimension. Conceptual sophistication is characterized by the implicit assumptions a person relies upon when considering the nature of chemical entites and processes in a given context.[13] These assumptions constrain thinking, and may also limit learning.[27] For example, Maeyer and Talanquer found that students exhibit several implicit assumptions about SPR in the context of chemical reactivity.[22] Some students relied on a macroscopic component-based implicit assumption that the ease of taking apart component pieces of molecules or reassembling them determines the favorability of a reaction. Considering bonds as physical objects that can be broken or formed makes it difficult to conceive of stability provided by resonance, which relies on a more sophisticated assumption that energetic stability is afforded by increasing available configurations. Using the Chemical Thinking framework, we explored the implicit assumptions that are present when students reason about relationships between chemical structures and spectroscopic properties.

Eye Tracking

We employed the use of eye tracking, a method of recording an individual's eye movements, in order to identify viewing patterns common to each identified implicit assumption. Measurements of eye movements are considered to be a good representation of visual attention. Hoffman and Subramaniam[28] have shown that if an individual's eyes are focused on an object, the individual's attention is also on that object. Additional research has shown that mental processing can be uncovered with eye movement data.[29−32] This research relies on two core assumptions: the *immediacy assumption* and the *eye-mind assumption*.[29] The immediacy assumption states that the viewer begins processing information being fixated on immediately and before moving to the next fixation. With each

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Table 1. Demographic Information about Study Participants

Educational Level (Abbr)	Male	Female	N	Course Enrolled in (End-of-Course grade Distribution)
First year (F)	4	5	9	General Chemistry II (4 A, 3 B, 1 C+, 1 C)
Second year (S)	4	3	7	Organic Chemistry I[a] (3 A, 1 A−, 1 B, 1 B−, 1 W)
Final year of studies (SR)	3	1	4	Quantum Mechanics[b] (1 A, 2 A−, 1 B−)
Graduate student (GS)	3	3	6	-
Total	13	12	26	-

[a]Participation in this study occurred after the unit on IR spectroscopy. [b]One student in final year of studies was not enrolled in any chemistry courses, end-of-course grade reported for this student is the course completed the semester prior (Inorganic Chemistry).

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, it can be inferred that commonly occurring eye gaze patterns might represent similar ways of processing a visual stimulus.

Eye tracking is a relatively recent addition to the chemistry education researcher's toolbox, with only a handful of studies having been published at the time of this writing.[33−42] Tang and Pienta used eye tracking to investigate the role of complexity factors in both stoichiometry[38] and gas law[36,41] problems. Another group of researchers used eye tracking to explore how students use ball-and-stick images versus electrostatic potential map images when presented with different types of questions about a molecule.[39,42] Stieff et al.[40] examined students' representational competence when looking at interactive animations used in molecular mechanics. In the current study, we use eye tracking, along with a think-aloud protocol, to examine how students look at the infrared (IR) spectra of two substances and relate the molecular structures of these substances to their respective IR spectra.

RESEARCH QUESTIONS

Students' understanding and reasoning about SPR have been studied extensively. However, an examination of the relationship between implicit assumptions and students' visual and cognitive focus has yet to be explored. This study addresses the following research questions:

1. What implicit assumptions appear to constrain the reasoning of students at different educational levels as they relate molecular structures and IR spectra?
2. What do eye gaze patterns reveal about chemistry students' assumptions about SPR when relating molecular structures and IR spectra?

METHODOLOGY

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 method was designed to elicit student thinking about relationships between molecular structures and IR spectroscopy.

Setting and Participants

Study participants were recruited from a medium-sized nontraditional university in the northeastern United States. The university's undergraduate population was 22.8% Asian, 17.5% Black/African American, 16.0% Hispanic/Latino, 1.2% Cape Verdean, 39.5% White, and 2.9% two or more races. Graduate student enrollment was less diverse, with 73% White and the balance primarily Asian or Black/African American. The participants in this study were representative of the diversity of enrollment of undergraduate and graduate students in the college.

We recruited students across educational levels in order to capture a range of experience and training in chemistry, particularly with respect to having studied spectroscopy. Spectroscopy is not studied in general chemistry (first-year). IR and other spectroscopic methods are studied in organic chemistry (second-year) and participants enrolled in that course were recruited after having been introduced to IR spectroscopy. Participants who were in their final year of undergraduate studies were enrolled in quantum mechanics, had already taken analytical chemistry and physical chemistry, and were engaged in a full-year chemistry research experience. All recruitment and study efforts were approved by the university's Institutional Review Board. Undergraduate student volunteers were recruited via announcements made in laboratory sections, and graduate students were recruited via a graduate student listserv. Table 1 shows the distribution of participants by chemistry educational level and gender.

Eye Tracking Apparatus

Eye movements were monitored with a Tobii X2-60 remote eye tracking system mounted to a 22-in. Dell monitor with a resolution of 1680 × 1050 pixels. The Tobii system uses pupil and corneal reflection tracking, in which a near-infrared illumination of the pupil is used to create reflection patterns on the cornea of the participant.[43−46] Two image sensors are used to capture images of the pupils and the reflection patterns. The software then uses an image-processing algorithm and a physiological 3D model of the eye to estimate the point of the participant's gaze.[43] The system has a sampling rate of 60 Hz. All participants were calibrated using a nine-point manual calibration before beginning the eye tracking. Tobii Studio 3.2.3 software was used to build the eye-tracking protocol, operate the eye-tracking hardware, and collect the eye-tracking data.

Data Collection

Each participant took part in one 30−60 min session. Sessions included eye tracking with a think-aloud interview and request of additional data, including demographic information.

While eye tracking creates a quantitative record of where participants are looking, it is not a reliable indication of what participants are thinking. Thus, it is common during eye-tracking protocols to collect other types of data in order to assist in interpretation of the results. A think-aloud protocol

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was used concurrently with eye tracking in order to capture participants' working memory responses directly. Think-aloud protocols have been used by previous authors in conjunction with eye tracking for investigating perceptual and attentional processes,[47,48] cued retrospective reporting,[35,49,50] and investigating the relationship between vision and speech over time.[51] Several authors have noted that the use of concurrent verbalizations can prove problematic, because the participant performs the task more slowly[52,53] and the increased cognitive load slows down eye movements and learning processes.[54,55] A benefit, however, is that the data sources are recorded simultaneously so they can be closely linked.[44] Think-aloud protocols provide an in-the-moment perspective, which has been shown to deviate from retrospective protocols.[56] Because the task was not time-dependent, the benefits of using a think-aloud protocol outweighed its potential problems.

Before the eye-tracking session, participants were given an explanation of think-aloud protocols and asked to make their responses as detailed as possible while explaining their thinking throughout the process. During the eye-tracking session, participants were asked to explain how the molecular structures of two compounds caused the peaks in their respective IR spectra (Figure 2). The interviewer did not speak during the eye-tracking session.

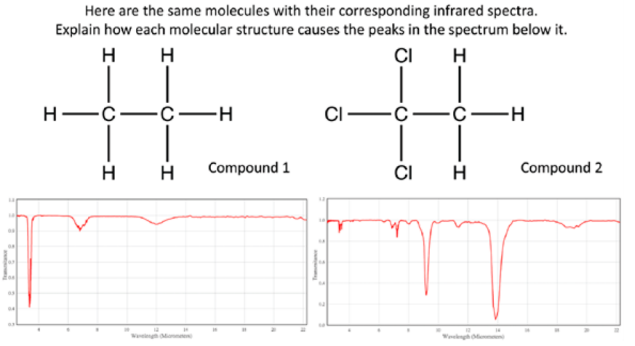

Figure 2. Students were given this visual stimulus and asked to answer the question aloud. The question asks participants to "Explain how each molecular structure causes the peaks in the spectrum below it." IR spectra were obtained from the NIST Chemistry Webbook.

Prior to collecting data with this instrument, several iterations of questions were piloted with both faculty and undergraduate students, who provided input on their comprehensibility, relevance for relating molecular structure and spectroscopic properties, and difficulty. The on-screen prompt was revised to adopt phrasing that triggered participants to respond during think-aloud interviews about how they related molecular features to IR spectra. The question was intentionally open-ended and participants were not time-restricted. The first author maintained control over advancing the slides and did so when participants indicated they had provided as complete an answer as they thought possible.

Qualitative Analysis

Audio recordings of participants' think-aloud sessions were transcribed to text verbatim. Transcripts were qualitatively coded,[57] first coding for primary thinking patterns and explanations of features in the IR spectra of each participant. Common codes were then grouped together into overarching themes and implicit assumptions were inferred from commonalities present. For example, two primary thinking patterns that were grouped into the same implicit assumption of "atoms as components" included "larger peaks result from atoms with higher atomic weight" and "the quantity of kinds of atoms accounts for the number of peaks". In contrast, two primary thinking patterns that were grouped into the implicit assumption of "bonds as components" included "energy absorption differs based on type of bond" and "particular bonds correspond to peaks in specific regions". A test of inter-rater reliability of 20% of the data initially yielded 67% agreement between the authors. We discussed the coding, came to 100% coding agreement, and revised the definitions, inclusion criteria, and exclusion criteria in the codebook. The remainder of the transcripts were then coded by the first author. Four months after the first author initially completed coding of the transcripts, both authors reviewed the codebook, excluding examples, and then all participant responses were coded independently by each author. Tests of inter-rater reliability resulted in a Cohen's κ of 0.88.

Quantitative Data Analysis

Raw data were transformed to fixation data by Tobii Studio 3.2.3 software. On the basis of accepted literature values, a fixation threshold of 100 ms was used.[36,37] With our 60 Hz instrument, each fixation is the result of roughly six data points. The colored regions in Figure 3 indicate the areas of interest

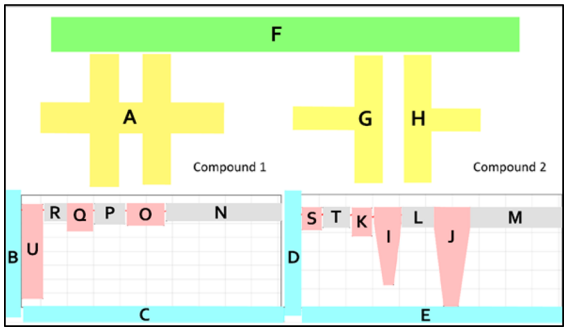

Figure 3. Researcher-defined AOIs for the question (green), molecular structures (yellow), IR spectra axes (blue), IR peaks (red), and IR baselines (gray).

(AOIs) in which data were collected. AOIs were designed with the research questions in mind, and were grouped by type: question (green), molecular structures (yellow), the spectra axes (blue), spectral peaks (red), and spectral baselines (gray).

Fixation sequences were analyzed using *eyePatterns*, an open-source software tool.[58] The "Pattern Finding" tool was used to identify fixation patterns of the collapsed sequences. In a collapsed fixation sequence, participants' multiple successive fixations within a single AOI are collapsed into a single gaze or dwell for the purposes of sequence analysis.[58] For example, the fixation sequence AAAAAGGHHHH would be collapsed to AGH. This enables focusing solely on the transitions between AOIs. We chose to identify patterns in fixation sequences which were three AOIs long based on suggestions from the literature that this is the maximum sequence that can be interpreted.[46,59] For each participant, a percentage of occurrence for each pattern type was determined by dividing the number of times the pattern type occurred by the total number of three-AOI sequences for that participant.

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RESULTS

Qualitative Findings

The qualitative coding resulted in the emergence of three implicit assumptions, which were termed: atoms-as-components, bonds-as-components, and bonding.

Participants whose reasoning exhibited an underlying assumption of atoms-as-components seemed to think about molecules as collections of atoms without considering how those atoms were connected or interacted with each other. These participants focused on the identities and quantities of individual atoms and how the presence or absence of particular atoms was related to the IR spectrum of the substance.

Participants who reasoned based on an underlying assumption of bonds-as-components still approached molecular structures as collections of components without regard to how those components interacted. However, these participants imagined the components as two or more atoms connected together, which they referred to as bonds (e.g., "the C−C bond") or functional groups (e.g., "the chlorine group, —Cl"). Often, they made note of which functional groups could be identified by the IR spectrum. Several participants referred to an IR spectrum as being like a "fingerprint of a molecule". Within their explanations there was no indication that these participants thought of bonds as anything more than a connection between two atoms, as if a bond were a labeled stick between specific atoms.

Finally, participants whose reasoning exhibited an implicit assumption of bonding most often spoke about interactions between energy and matter, and referred to relationships that were altered between atoms or regions of molecules. These participants made specific reference to relationships between intramolecular forces and the respective IR spectra of the molecule. They reasoned about how atoms with larger or smaller masses, or bonds with greater or lesser polarity, would influence the energy necessary to excite bond vibrations. Many of these students also reasoned based on the mechanism of IR spectral responses resulting from changing dipole moments that occur when particular vibrational modes are induced.

Figure 4 shows the percentage of participants within each educational level who were coded as reasoning based on atoms-as-components, bonds-as-components, or bonding assumptions. As indicated in the figure, students at increasing educational levels had fewer atoms-focused explanations and more bonding-focused explanations.

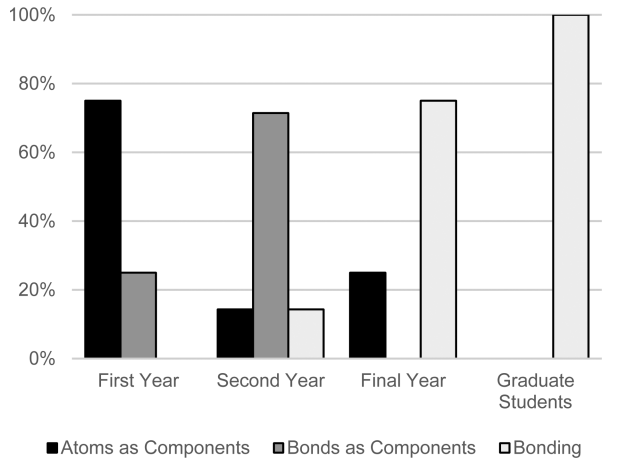

Figure 4. Distribution of implicit assumptions by educational level.

"Atoms-as-Components" Assumption

The atoms-as-components assumption was present in 32% (n = 8) of participants. Explanations using this implicit assumption varied in the way in which they were used, with participants talking about atoms by quantity, type, molecular weight, and electronegativity. These atoms-focused explanations were most common among first-year students, with 75% (n = 6) of these students demonstrating this assumption. For example, one first-year student explained the differences in the spectra based on the differences she was able to observe in the atomic composition of the molecules:

> ***F7:****...I think that's because it [Compound 1] 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 was trying to reason logically about a phenomenon that was new to her (i.e., IR spectroscopy) using explicit cues from the molecular structures, namely elemental composition. Another first-year student made a similar remark when she talked about the molecules and their spectra, but instead 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 available in the molecular structure to explain a phenomenon that she did not fully understand. One student in the final year of his undergraduate studies also reasoned with this logic-based approach, though he displayed vocabulary (e.g., "shift") that was likely absorbed from studying spectroscopy:

> ***SR4:*** *I think the reasoning for compound one is because of the hydrogen atoms and how that would all relate to that and that smaller peak. But with compound two it would have the chlorine atoms causing those large peaks and... Hm. Yeah, probably it causes, the one on the left [compound one] would be from the hydrogen and the one on the right [Compound 2] would be from the chlorines and that probably causes a shift.*

"Bonds-as-Components" Assumption

A bonds-as-components assumption was present among 28% (n = 7) of participants. Some students who relied on this assumption made associations between bonds within the molecule and specific peaks in the spectrum. For example, one second-year student explained:

> ***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 identifying the peaks. While she may be relying on correctly memorized bond-peak associations, her response does not demonstrate an understanding of *why* certain peaks are associated with specific structural features.

Another second-year student who relied on a bonds-as-components assumption invoked knowledge of IR spectra from

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class, stating that IR spectra are about functional groups. She 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 available explicit cues provided by the different element symbols in the molecular structures, resulted in conflicting conclusions, as evidenced by this train of thought: (1) IR peaks show functional groups; (2) the differences in the peaks must arise from the differences in the presence or absence of bond-paired atoms; (3) the presence of chlorine bonded to carbon in Compound 2 is the only difference between the compounds; therefore, it must be causing the peaks that are different; but (4) chlorine is not a functional group, therefore, it should not show up in an IR spectrum. In the end, she reconciled the discrepancies by reasoning, "even though that's not a functional group", concluding that something in her knowledge bank must be incorrect.

"Bonding" Assumption

The bonding assumption was present in 40% of participants (n = 10). Participants in the uppermost educational levels displayed the most advanced conceptual sophistication, as indicated by their responses cuing on types of vibrational motion, rotation, symmetry and dipole induction, and energy absorption.

Of particular prevalence among students in this group 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. For example, GS4 noted:

> ***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 though, most graduate students also pointed out an explicit requirement of IR spectroscopy: the vibrational motion must induce 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 apparent to all chemistry educators and education researchers: with more advanced content knowledge comes an ability to better understand molecular structures and to interpret IR spectra. While inspection of think-aloud transcripts provided useful information for inferring assumptions that shape SPR thinking, the think-aloud protocol did not allow for gathering additional cognitive information from participants, specifically what cues they paid attention to and how they connected them while reasoning. Therefore, analysis of quantitative eye-tracking data was undertaken to further uncover patterns of viewing that corresponded to specific implicit assumptions.

Quantitative Analysis

Eye fixation sequences can reveal perceptual strategies that people develop for interpreting visual stimuli.[33,46,60] 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-AOI sequence, where the AOIs are represented by the letters A through U (see Figure 3). Analysis of the collapsed sequence data revealed a total of 1032 unique sequences that were three AOIs in length. Of these, we chose to eliminate sequences that occurred only once among the 26 participants, reasoning that such sequences were likely the result of the participants randomly searching the visual stimulus. Additionally, these excluded sequences might also represent transition states from one type of thinking to another (e.g., from "what is similar about these structures" to "what is similar about these spectra"). After removing these data, there were a total of 299 three-AOI sequences that remained. These sequences were grouped according to the types of AOIs they included. The resulting identified patterns, including their descriptions and examples, are given in Table 2.

Table 2. Patterns Resulting from Analysis of 3-AOI Sequences[a]

Pattern	Description	Examples
1	Only look at molecular features	*AGH, GHG*
2	Return to the question	*AFA, FGH*
3	Look at molecular features and spectra	*HGI, JHG*
4	Look at molecule, spectrum, and axis	*AUB, JEG*
5	Look at a spectrum and an axis	*QCQ, IDJ*
6	Look only within spectra	*SKI, UIJ*
7	Look only at spectra axes	*BCB, DEC*
8	Patterns which indicate random searching	*BCA, ASC*

[a]Note: Refer to Figure 3 for AOI labels.

Analysis by Assumption. Figure 5 shows the percent occurrence of each sequence pattern type sorted by assumption. Percent occurrence is indicative of the average frequency of the pattern type for each participant, not the number of participants using the pattern. Tables showing which pattern types were present for individual students can be found in the Supporting Information.

When comparing students with an atoms-as-components assumption to those with a bonding assumption, it is evident that different types of viewing patterns were used. Students who relied on an atoms-as-components assumption had the highest occurrences of Patterns 1, 2, and 4 sequences. Students whose reasoning was built on the more sophisticated bonding assumption had the highest occurrences of Patterns 5 and 6. Patterns 7 and 8 were negligible for all groups. Students who relied on a bonds-as-components assumption were less clear-cut. Although Pattern 3 was present for all students, it is most prevalent among the bonds-as-components students. Generally,

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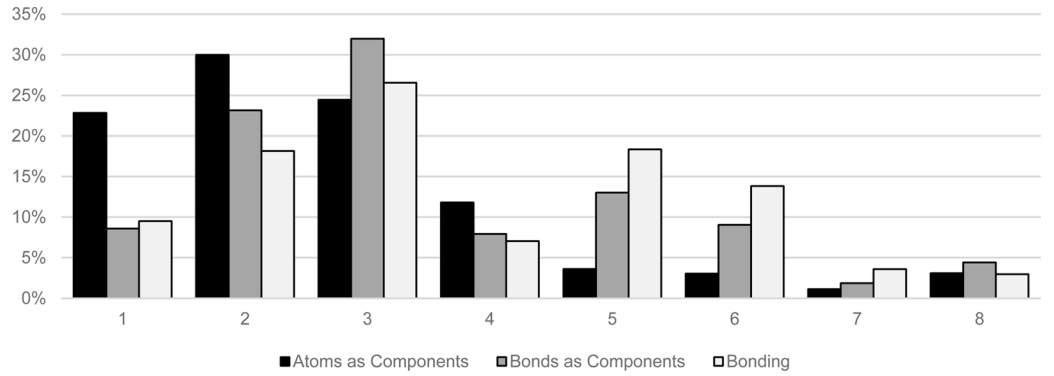

Figure 5. Percent occurrence of sequence pattern types sorted by student assumption types.

a shift from more emphasis on the component features of molecules (Patterns 1 and 2) toward more relating certain spectral features to molecules (Patterns 5 and 6) occurs.

DISCUSSION

The aim of this study was to examine how the eye gaze patterns of students correlate to their implicit assumptions about SPR, where IR spectroscopy was the property of interest. The following section presents inferences drawn from synthesis of the findings of the identified implicit assumptions and their associated gaze patterns.

Correlation between Eye-Tracking and Qualitative Findings

Progress in the development of thinking about molecular structures and the associated IR spectra of those substances appears to occur with increasing sophistication according to educational level. At lower conceptual sophistication, students cued on the types of atoms that comprise a molecule, and paid particular attention to how many of each atom type were present in the molecular structure. Students who relied on this atoms-as-components assumption envisioned molecules to be agglomerations of atomic components that individually give rise to properties in an additive fashion. For example, students explained that spectral peaks are associated with the presence or absence of atoms, or atom types, in the molecule. This assumption was most prevalent among first-year students (n = 6 of 8). In the absence of having learned formally about IR spectroscopy, students reasoned based on knowledge about atoms, cued by the elements in the molecular structures. Students' reasoning was based on properties of the component atoms, such as atomic mass and electronegativity.

The eye-tracking data provided further support for an atoms-as-components assumption underlying the reasoning of these students. Pattern 1, where students only viewed AOIs of the molecules in the three-AOI sequence, had the highest occurrence among students with this assumption. The prevalence of Pattern 1 indicates these students were primarily comparing the structural and compositional features of ethane and trichloroethane, presumably in order to identify differences that would allow them to formulate a reasonable explanation for the observed spectral features. Also present among the highest-occurring viewing patterns for this group was Pattern 2, in which students returned to the question. Tang and Pienta[36] observed similar results, noting that students who were unsuccessful at solving a gas law problem had a higher occurrence of fixations on the question.

Progression to more advanced conceptual sophistication appears to be evidenced by a shift to a more structural view, associating bond types with features of the IR spectrum. The qualitative data suggested that students who rely on a bonds-as-components assumption view bonds as individual components with independent properties. Thus, students continue to see molecules as agglomerations of components, as above, but now the components are bonds. The assumption appears to limit reasoning to the identification of the presence or absence of bonds, which permits labeling specific spectral peaks with particular bond types. Most second-year students among the participants (n = 5 of 7) appeared to reason based on the bonds-as-components assumption. The second-year chemistry course, organic chemistry, uses a textbook that presents a typical approach to teaching IR spectroscopy:[61] "IR remains an important tool because of its usefulness in identifying the presence of certain *functional groups* within a molecule" (p 574). Hence, it was not surprising that many students explained that an IR spectrum is a "fingerprint of a molecule".

The eye-tracking data revealed that students who held a bonds-as-components assumption had the highest prevalence of Pattern 3. This seems to indicate the students who relied on this assumption: (1) understood that IR spectra are related to molecular structures, and (2) tried to relate specific peaks to particular structural features. Among second-year students, the primary comparisons of this type occurred for the two large peaks of the spectrum of Compound 2 (AOIs I and J, Figure 3), indicating students may think molecular differences show up as the largest peaks in the spectra.

Students whose reasoning was based on a bonding assumption appeared to be released from thinking of molecules as collections of components, whether atoms or bonds. Instead, they discussed a more holistic view of molecular structures, explaining how features of the IR spectrum arise based on a molecule's structure. Rather than spectral peaks correlating to the presence or absence of components, these students explained correlations to light-matter interactions.

Students with a bonding assumption exhibited the highest occurrence of Patterns 5 and 6 in the eye-tracking data, although Pattern 3 accounted for 27% of all three-AOI sequences for this group. Usage of the Pattern 5 sequence indicates participants were identifying whether peaks occurred in typical wavenumber regions, which some of the participants had likely committed to memory. However, the presence of this pattern also corroborates the think-aloud data in which some participants reasoned about why some vibrational excitations required greater or lesser energy. Similarly, Pattern 6 sequences involved looking only at spectral features, suggesting that the

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students were trying to interpret peaks relative to each other, a more advanced tactic in interpreting IR spectra.

Directions for Future Research

This progression of conceptual sophistication in students who experienced a traditional undergraduate chemistry curriculum is aligned with the results of prior research.[4,22,23] The least conceptually sophisticated assumption, atoms-as-components, involved cueing on explicit structural features, and often involved the application of simple associations in reasoning about how molecular structures account for IR spectral features. The bonds-as-components assumption appears to mark a transition toward more sophisticated thinking. While students cued on explicit features (atom combinations and bonds between them), they started to recognize functional groups (an implicit idea). The bonding assumption, however, marks a clear shift to mechanistic reasoning. Students who relied on the bonding assumption were also found to reason through different premises (e.g., higher-energy photons induce vibrational transitions in stronger bonds, vibrations in bonds between lighter atoms have higher frequencies) to explain how spectral features result from bonding arrangements in a molecular structure.

In future research, it would be interesting to compare these results to the progression of conceptual sophistication in SPR thinking in students who have experienced a nontraditional undergraduate chemistry curriculum. For example, the *Chemical Thinking* general chemistry (first-year) curriculum[62] teaches the mechanism of IR spectroscopy in the first semester of general chemistry, and engages students in inferring molecular structures that are consistent with IR spectra and mass spectrometry evidence. Perhaps students who experience such a curriculum would demonstrate reliance on the bonding assumption earlier, and might develop more mechanistic and premise-based reasoning that may be activated in other problems in chemistry.

Limitations of the Study

While the data are suggestive of trends, the number of participants was insufficient to reach statistical significance in comparisons between educational levels or between implicit assumptions. In the quantitative analysis of the eye-tracking data, some of the AOIs were not ideally spaced to avoid overlap. In the case of two closely adjacent AOIs (particularly B and U in Figure 3), there was the possibility that a student may have been looking at one of the AOIs but was recorded as looking at a different one. Additional studies that wish to employ eye-tracking methods should take care to design visual stimuli so that AOIs are clearly distinguishable.

CONCLUSIONS

This work demonstrates that analyzing the sequences of fixations during eye-tracking can provide useful information about what students are thinking when relating molecular structures to spectroscopic responses, and that this information goes beyond what can be learned from think-aloud interviews. In particular, we showed that patterns of viewing differed depending on the implicit assumptions students made about how spectroscopic responses are related to molecular structures. We observed three primary assumptions, corresponding to logical reasoning about properties of atoms in the absence of understanding what spectroscopy is (atoms-as-components assumption), considering spectra as fingerprints of molecules (bonds-as-components assumption), and reasoning about the spectroscopic response based on the interaction of matter and energy (bonding assumption). Being mindful of these three primary assumptions can aid chemistry instructors to interpret their students' responses in formative assessment, such as asking clicker questions, and may provide instructors with novel ideas for how to ask students questions to probe their thinking.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00529.

Tables showing the presence of pattern types (PDF)

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Notes

The authors declare no competing financial interest.

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