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Multidimensional Pattern Recognition in High-Resolution 2D and 3D Spectra of Gas-Phase Molecules

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Peter C. Chen*

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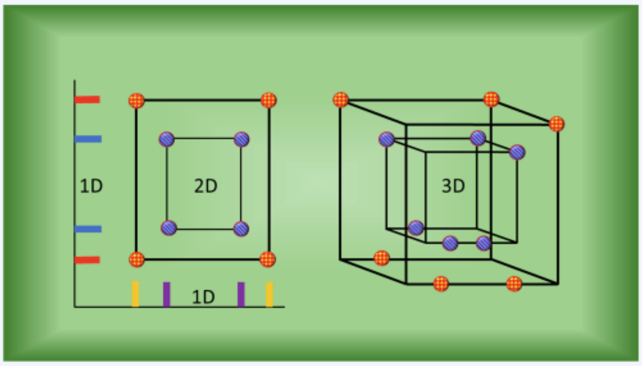

CONSPECTUS: When molecules transition from the condensed phase to the gas phase, their spectra undergo a dramatic transformation as well; each peak in a condensed-phase spectrum can yield thousands of peaks in the gas phase because the molecules are free to rotate and those rotational motions are quantized. These gas-phase spectra contain a wealth of detailed information about molecular structure and behavior, but peak densities are often so high that congestion obscures the patterns needed to assign peaks and extract molecular constants. This Account describes how coherent multidimensional techniques not only reduce peak densities and congestion in gas-phase spectra but also create multidimensional patterns that are easy to recognize and interpret. First, all peaks with the same vibrational quantum numbers form rotational patterns such as X's, double parabolas, and asterisks. These rotational patterns are composed of basic units and can provide immediate information about the molecule's structure, behavior, and rotational selection rules. Second, groups of these rotational patterns can be arranged into vibrational patterns that form arrays of rectangles or parallelograms. These vibrational patterns can be used to determine wave-mixing processes and measure vibrational constants. Coherent multidimensional spectroscopy therefore automatically separates vibrational and rotational information and then sorts peaks by vibrational and rotational quantum number. Furthermore, if the sample is composed of a mixture, then these patterns can also sort peaks by species, and higher-dimensional techniques can even provide the ability to select a species in the mixture. These techniques have successfully produced highly patterned 2D and 3D spectra for samples that otherwise generate patternless spectra such as isotopologue mixtures and vibronically perturbed molecules such as NO_2.

High densities of states can lead to congestion and perturbations that make it difficult to accurately assign peaks using the information that is traditionally available from 1D spectra: a peak's intensity and its frequency. Coherent 2D and 3D techniques are well-suited for dealing with and learning from perturbations because the coordinate of each peak in multidimensional space includes multiple frequency values. Accurate assignments are possible when peaks in 2D or 3D spectra that are perturbed along one frequency axis are unperturbed along an orthogonal frequency axis. Furthermore, patterns often repeat in adjacent rows or columns, so regions that are less congested can be used to resolve or identify key peaks or patterns in regions that are severely congested. Perturbations can make the spacings within multidimensional rotational and vibrational patterns slightly irregular, but these automatically generated patterns remain easy to recognize and analyze.

This Account describes three high-resolution coherent multidimensional spectroscopy techniques, the types of patterns they can produce, and how information can be extracted from these patterns. This work is being conducted at Spelman College, a historically Black college for women where all of the students are undergraduates. The resulting techniques are not only highly effective for dealing with some of the most congested, perturbed, and challenging spectroscopic systems, but they are relatively easy to use, moderate in price to set up, and quick to run.

KEY REFERENCES

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one-dimensional spectra appear patternless due to a series of conical intersections. HRC2DS can use assigned peaks in one dimension to assign peaks in a different dimension.

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- Wells, T. A.; Muthike, A. K.; Robinson, J. E.; Chen, P. C. High Resolution Coherent Three Dimensional Spectroscopy of NO_2. *J. Chem. Phys.* **2015**, *142*, 212426.[3] *This article demonstrates how HRC3DS is effective for studying molecules with severe spectral congestion and energy levels that are widely perturbed.*
- Daniels, D. A.; Wells, T. A.; Chen, P. C. High Resolution Two-Dimensional Infrared (HR-2DIR) Spectroscopy of Gas Phase Molecules. *J. Chem. Phys.* **2022**, *157*, 184201.[4] *This paper describes the new HR-2DIR technique and includes proof-of-principle results.*

■ INTRODUCTION

Pattern recognition has long played a major role in the interpretation of spectra. For example, patterns containing nearly evenly spaced peaks can be signatures of vibrational progressions or rotational bands, leading to peak assignments and details about molecular structure and behavior. Unfortunately, many of the patterns in gas-phase molecular spectra are buried by congestion from large numbers of overlapping rotational−vibrational peaks; gas-phase molecular spectra can contain thousands or even millions of peaks that are overcrowded in very limited space on a one-dimensional spectrum. This congestion obscures the patterns needed to assign peaks by quantum number. Furthermore, Coriolis interactions, Fermi resonances, torsional motion, state mixing, and other effects can perturb peak intensities and positions, making pattern recognition and interpretation difficult. The presence of isotopologues, isotopomers, and conformers can further complicate or obscure patterns. Molecular jets[5] cryogenically cool molecules to reduce congestion by eliminating most of the rotational peaks. However, they also cause a loss of rotational information, and many studies need to be carried out at higher temperatures. And while molecular jets are highly effective at reducing congestion, more powerful tools are needed for dealing with perturbations.

This Account describes the development of high-resolution coherent multidimensional spectroscopy (HRCMDS), a group of spectroscopic techniques designed to overcome spectral congestion in gas-phase molecular spectra. HRCMDS replaces congested, patternless regions in 1D spectra with rich, multidimensional patterns that provide more information on molecular structure and behavior. This Account describes three major HRCMDS techniques and the unique patterns they can produce. First, high-resolution coherent 2D spectroscopy (HRC2DS) is a relatively simple technique suitable for small molecules that converts patternless 1D spectra into highly patterned 2D spectra. Next, high-resolution coherent 3D spectroscopy (HRC3DS) expands that capability to a third dimension, making it useful for further removing spectral congestion expected for larger, more complicated molecules and mixtures. Finally, high -resolution two-dimensional infrared spectroscopy (HR-2DIR) is a new technique that produces new kinds of patterns in the infrared region.

■ BACKGROUND

Multidimensional spectroscopy can effectively overcome congestion problems by expanding the space available for peaks to reside, resulting in lower peak densities and less peak crowding. New information based upon the relationship between peaks lies in the off-diagonal region of a multidimensional spectrum. For example, a peak located at the position x, y in a 2D infrared spectrum could indicate that there are two vibrational modes that are coupled, one at x frequency and the other at y frequency.

The rotational motions of gas-phase molecules are robust and do not couple the way that vibrational motions do. Instead, rotational peaks in multidimensional spectra may indicate resonances that have a common upper or lower level and therefore also have common quantum numbers. Rotational selection rules such as $\Delta J = \pm 1$ or $\Delta J = 0, \pm 1$ produce peaks that assemble into easily recognizable shapes (e.g., X's and asterisks) where the peaks are automatically sorted by quantum number and species. In fact, 2D plots such as those produced using Loomis–Wood software[6−8] have long been created to identify patterns from congested 1D spectra, but in HRCMDS spectra, 2D patterns appear automatically. A simple way to generate highly patterned 2D spectra is to use two-dimensional laser-induced fluorescence (2D LIF),[9−13] where the excitation source and detection wavelengths are both scanned so that their wavelengths comprise orthogonal y and x axes. HRCMDS is even more powerful because it provides greater control, more options (e.g., 3D spectroscopy), and is universal (i.e., the molecules do not need to fluoresce).

HRCMDS has been under development for approximately 20 years. In 2003, Suzuki and Tanimura published a theoretical paper predicting possible changes in rotational patterns if one were to develop a purely rotational coherent 2D spectroscopy technique for rotating gas molecules.[14] During that year, we began using visible laser beams to record the first rotationally resolved coherent 2D spectra in samples of freely rotating gas molecules. Since then, other research groups have recorded purely rotational 2D spectra of freely rotating molecules in the terahertz region[15,16] and 2D spectra of quasifree rotators in the IR region.[17]

Our HRCMDS techniques rely upon purely coherent four wave mixing (FWM) resonances rather than excited-state populations. The techniques work for all gas-phase molecules and levels, including those that are difficult to populate due to predissociation or conical intersections. They have been highly effective at generating easily recognizable multidimensional patterns for molecular systems that have previously yielded patternless 1D spectra and that have long resisted analysis. These systems include mixtures of isotopologues[18] and molecules that are heavily perturbed by multiple conical intersections.[1,3] The patterns that are created may be divided into two categories: rotational patterns and vibrational patterns. A rotational pattern consists of peaks that all have the same vibrational quantum numbers but different rotational quantum numbers, distributed into shapes such as X's, parabolas, or asterisks. Each rotational pattern is composed of several basic units, such as rectangles or triangles. The shape of rotational

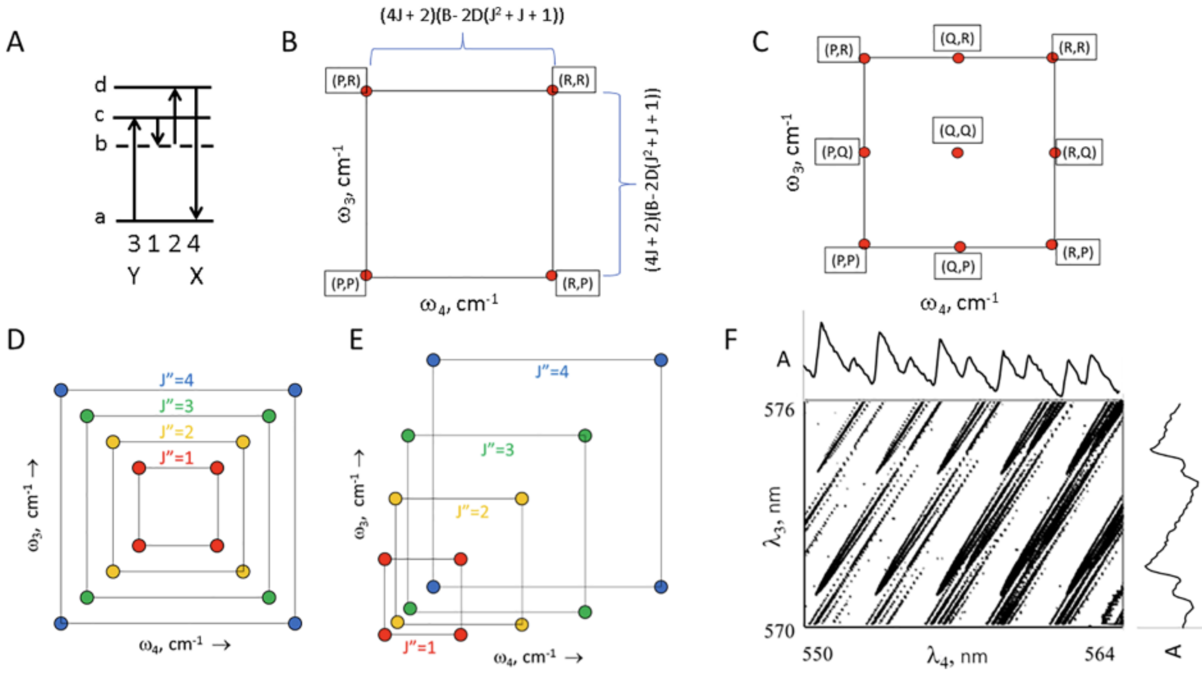

Figure 1. (A) FWM energy-level diagram, (B) rotational basic unit for $\Delta J = \pm 1$, (C) rotational basic unit for $\Delta J = 0, \pm 1$, (D) rotational pattern when $B' = B''$, (E) rotational pattern when $B' \neq B''$, and (F) HRC2DS spectrum of iodine (reprinted with permission from ref 30; copyright 2006 American Chemical Society) with the corresponding 1D absorption spectra above and to the right. Iodine's vibrational pattern shows vertical and horizontal alignment among the parabolas, which is consistent with that in Figure 2A.

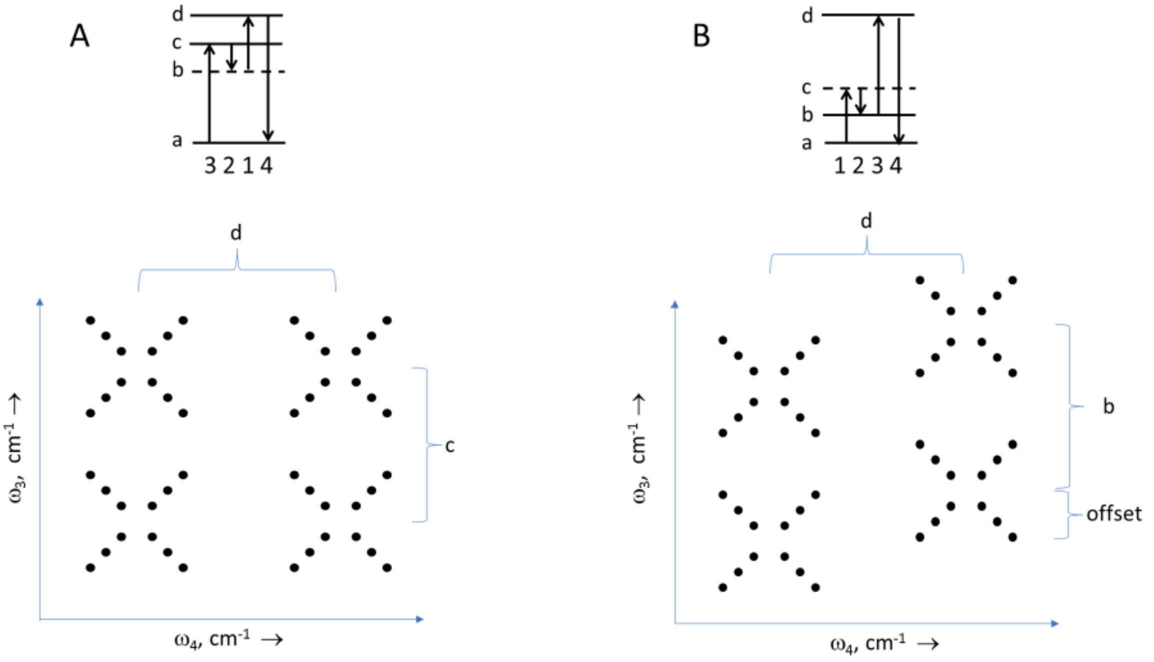

Figure 2. Vibrational patterns show the relative positions of rotational patterns (X's). The braces indicate the levels that determine the indicated spacing. For A, level a is common to $\omega 3$ and $\omega 4$, and levels c and d each contain multiple vibrations that are roughly evenly spaced. The spacings between X's along the x axis and y axis match the spacing between vibrational levels represented by levels d and c, respectively. For B, level d is common to $\omega 3$ and $\omega 4$, and the spacings between X's along the x axis and y axis match the spacing between vibrational levels represented by levels d and b. However, offsets are introduced along the $\omega 3$ axis because it is not resonant with ground level a. These offsets depend upon the differences between vibrational frequency spacings in level b and those in d. Adapted with permission from ref 31. Copyright 2010 American Chemical Society.

patterns depends upon factors such as the rotational selection rules, the FWM process, the laser frequencies that are scanned, and the spectrum's axes.

The use of two or three separately controllable input beams of coherent light provides the ability to select the levels being probed and to design different kinds of HRCMDS techniques. For example, if three independently tunable laser beams are used, then the generated FWM beam frequency can equal the sum of any two input laser frequencies minus the frequency of the third (Figure 1). The resulting multidimensional spectra can probe up to four different energy levels and can be displayed in up to four dimensions. Phase matching can also be used to control which input frequencies are added or subtracted and which levels are probed.

Figure 1A shows an FWM energy-level diagram that can be used to generate coherent 2D spectra. An intense, coherent beam of light (photon 4) is generated by this FWM process when three intense coherent input beams (photons 1, 2, and 3) are focused and overlapped in a sample and the phases of the light fields are matched. As the frequencies of photons are scanned across molecular resonances represented by the solid horizontal lines, the intensity of the generated fourth beam grows and falls, producing peaks in the spectrum. To generate a multidimensional spectrum, two or more of these photon frequencies are scanned across real levels, represented by levels c and d.

Figure 1B,C shows examples of rectangular basic units formed by peaks that have the same ground-state rotational quantum number J''. Figure 1B has $2 \times 2 = 4$ peaks produced by rotational selection rule $\Delta J = \pm 1$, and Figure 1C has $3 \times 3 = 9$ peaks produced by $\Delta J = 0, \pm 1$. The x, y coordinate labels for each peak correspond to P for $\Delta J = -1$, R for $\Delta J = +1$, and Q for $\Delta J = 0$. The size of each basic unit increases with the value of J''. For the $J'' = 0$ basic unit, the peaks with a P label will be missing because J cannot be negative. If the rotational constant B'' for the lower level is the same as B' for the upper level, then the rectangles will be concentric and the resulting rotational pattern will be X-shaped for $\Delta J = \pm 1$ (Figure 1D). If $\Delta J = 0, \pm 1$, then the resulting rotational pattern resembles an asterisk. If $B' \neq B''$, then the centers of the rectangles will shift and the arms of the X will be curved into a double-parabola pattern (Figure 1E). In Figure 1F, the parabolas' shift toward longer wavelength indicates that $B' < B''$ and that iodine's bond length increases when going from the ground to the excited state.

When multiple rotational patterns with different vibrational quantum numbers appear in a multidimensional spectrum, their relative alignment produces a vibrational pattern. These vibrational patterns are 2D equivalents of vibrational progressions in electronic spectroscopy. For example, if the rotational pattern is an X, then multiple X's may form an array where they appear ordered by their vibrational quantum numbers v. If the FWM process is the one shown in Figure 2A and the spectrum has frequency ω_4 on the x axis and ω_3 on the y axis, then a separate row of X's will be produced by each v' value for level c and separate columns of X's will be produced by different v' values for level d. The rows and columns in this rectangular vibrational pattern will be arranged sequentially by the vibrational quantum numbers for levels c and d. Figure 2B shows a different vibrational pattern from a different FWM process where the X's form diagonal lines instead of rows and the resulting vibrational pattern is a parallelogram. These two FWM processes generate light in the same region of the spectrum ($\omega 4 = \omega 1 - \omega 2 + \omega 3$), so the vibrational pattern helps to identify which FWM process is responsible for producing the peaks in the spectra.

Having separate vibrational and rotational patterns in HRCMDS spectra facilitates the separation of vibrational information from rotational information[19] and enables new strategies for dealing with congestion and perturbations. Within one rotational pattern, all of the peaks have the same vibrational quantum numbers for all of the real levels in the FWM diagram. The dimensions of basic units along both axes are useful for obtaining rotational constants and quantum numbers[20] for each axis of the multidimensional spectrum. The spacing between rotational patterns equals the spacing between vibrational levels in either the upper or lower state. For 2D spectra that are highly congested, the high level of redundancy among both rotational and vibrational patterns makes it possible to use peaks in less-congested areas to find the correct corresponding peaks in highly congested areas. Perturbations that alter the position of peaks along one axis can be handled by using the affected peak's position along an orthogonal unperturbed axis. Rotational patterns can remain easily identifiable despite conical intersections that cause vibronic mixing and irregular spacings between vibrational patterns. And since one axis might be perturbed while the other is not, peaks previously assigned in one region can be used to assign peaks in perturbed or heavily congested regions. These unique capabilities have been demonstrated by locating and assigning peaks in NO_2, which is notorious for its lack of rotational and vibrational patterns due to multiple conical intersections.[1,3]

■ HIGH-RESOLUTION COHERENT 2D SPECTROSCOPY

HRC2DS was originally discovered by simultaneously scanning the wavelength of a narrowband tunable OPO and the detection wavelength while generating FWM signals in flames.[21] Originally called coherent 2D resonance Raman spectroscopy and later 2D coherent double-resonance electronic spectroscopy, HRC2DS now describes a simple, general approach for generating rotationally resolved two-dimensional electronic spectra of gas-phase molecules: two or three beams are focused and overlapped in time and space, and the intensity of the FWM signal is monitored and scanned while also scanning the frequency of the detector and one of the input beams. Figure 3A,B shows two different FWM processes that have been used for HRC2DS, and Figure 2 shows the vibrational patterns they can produce if the intensity of the generated FWM beam is plotted as a function of the third and fourth photon frequencies (ω_3 and ω_4). The vibrational patterns appear in this kind of 2D

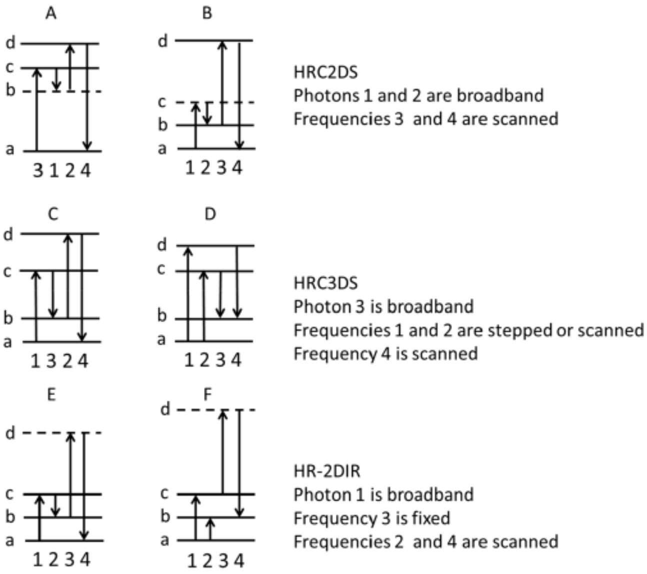

Figure 3. Six examples of FWM energy-level diagrams for three different HRCMDS techniques. The numbers on the bottom are labels for the photons, and the letters on the left of each are labels for energy levels.

spectrum because levels a and b are in the ground electronic state and levels c and d are in an excited electronic state, so photons 3 and 4 can connect a progression of vibrational levels in the ground electronic state to a progression of vibrational levels in the excited electronic state. The vibrational pattern is useful for determining which FWM process is responsible for creating the observed pattern.

The other two photon frequencies (ω_1 and ω_2) are produced by a single near-infrared broadband source such as an OPO that has been tuned to its degeneracy point ($\omega_{\text{signal}} = \omega_{\text{idler}}$). A simple and effect strategy is to use a single degenerate OPO beam containing both the signal and idler where all input beams are aligned on a single optical axis, a process called collinear phase matching. Optical filters are useful for combining the input beams and removing them from the output beam before detection. The use of at least one broadband input beam causes the output beam to contain multiple wavelengths which facilitates rapid multiwavelength detection using a monochromator equipped with an array detector. Using a 1 s integration time with a 2000 pixel CCD detector, this multichannel detection approach shortens the total acquisition time for a 2000 × 3000 point spectrum to 3000 s. The instrumentation is relatively simple and consists of four main components (Figure 4): a pump laser (e.g., Nd:YAG laser), a tunable narrowband laser (e.g., dye laser), a broadband source (e.g., OPO tuned to its degeneracy region), and a high-resolution monochromator with a CCD. All the techniques described in this Account were created, tested, and developed in an undergraduate research laboratory at Spelman College, a historically Black college for women. Spelman does not have a graduate program, so the instrumentation, techniques, and experiments involved in this work were designed to be run by undergraduate research students. Nanosecond lasers are relatively easy for undergraduate students to operate, and their narrow line widths make them convenient for acquiring high-resolution frequency domain gas-phase spectra.

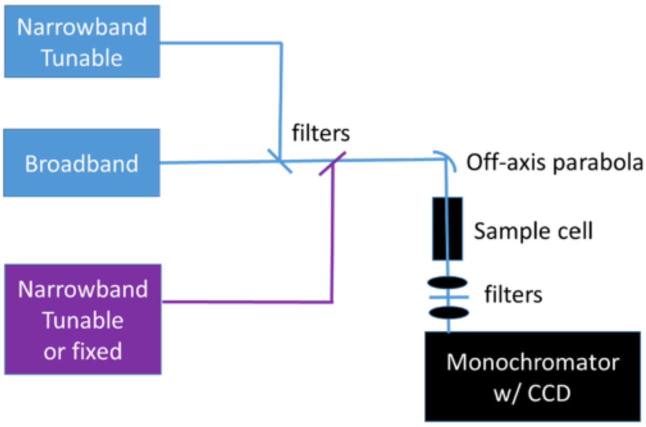

Figure 4. Simplified experimental diagram for an HRCMDS spectrometer. All input pulses arrive at the sample at the same time. To record a 2D spectrum or a 2D slice of a 3D spectrum, both the monochromator wavelength and one of the narrowband tunable sources are scanned. HRC2DS requires only two input sources (the blue components): a narrowband tunable source and a broadband OPO. For HR3DS, a second tunable source is added (purple component), and one tunable source is scanned while the other one is stepped. For HR-2DIR, both blue components are in the infrared region, and a fixed-wavelength visible beam is added (purple component) so that the output beam is in the visible region.

When analyzing HRC2DS spectra, it is often useful to identify possible common levels for the FWM process and scan. For the FWM process and scan shown in Figure 1, level a is the common level for photons 3 and 4. Therefore, the differences in the size of successive rectangles within a rotational pattern are due to changes in the value of J for levels c and d, and the differences in the size of any two adjacent rectangles are approximately equal to 4 times the rotational constant ($4B$) in the excited state (i.e., $4B_d$ along the x axis and $4B_c$ along the y axis) if the molecule behaves like a rigid rotor. Figure 1B includes the dimensions for each side when centrifugal distortion is included.

The common level is also useful for obtaining vibrational constants. For the FWM process and scan shown in Figures 2A, the vibrational constant ω_e for levels c and d can be approximated by measuring the difference in vertical and horizontal positions between rotational patterns; the vertical spacings match the spacings between the vibrational levels of c, and the horizontal spacings match the spacings between the vibrational levels of d.

HIGH-RESOLUTION COHERENT 3D SPECTROSCOPY

HRC2DS significantly reduces spectral congestion, but persistent peak congestion in 2D spectra can hinder the ability to assign peaks correctly. Furthermore, spectral congestion is typically more severe for larger molecules. For a sample containing a mixture of species, the rotational and vibrational patterns make it possible to group related peaks by species, but congestion can cause inaccurate peak identification. HRC3DS can eliminate spectral congestion by using a third dimension to reduce peak density.[22] It also can provide control over which species in a mixture produces patterns. In order to generate an HR3DS spectrum, an additional tunable narrowband laser or OPO is added to an HRC2DS setup to provide three frequency axes: two narrowband tunable source frequencies plus the detection frequency (Figure 4). One of the two independently tunable sources can be fixed on a resonance to select a specific species in the mixture and/or a set of quantum numbers so that the 2D slice that is produced by scanning the other tunable beam and the detection system contains only peaks or patterns from the selected species in a mixture.[23] Figure 5 shows that the basic unit is a triangle.

Figure 6 shows a cartoon of how basic units form the general rotational pattern in an HRC3DS spectrum. The peaks are represented by spheres, and the selection rule is $\Delta J = \pm 1$. This figure is an oversimplification because the actual peak positions depend upon the FWM process, but it illustrates how the basic unit for the 3D rotational pattern consists of six peaks that form a pair of (similarly colored) triangles on parallel planes and how these triangles' sizes and spacings increase as J'' increases. This growth is analogous to that for the rectangles in HRC2DS, shown in Figure 1D,E. In order to record a 3D spectrum that captures this complete 3D rotational pattern, one would need to record multiple 2D plots and then stack them to make a 3D spectrum. Each of these 2D plots serves as a 2D slice through 3D space, and some of the slices will contain triangles such as the ones shown in Figure 5.

The 2D slice shown in Figure 5 happens to contain two triangles. It illustrates how spectral congestion can be eliminated by expansion to the third dimension where the peak density is very low. Even though the frequency of the added (fixed) tunable laser beam was simultaneously resonant with two "unresolved" peaks in that dimension, Figure 5 shows that the

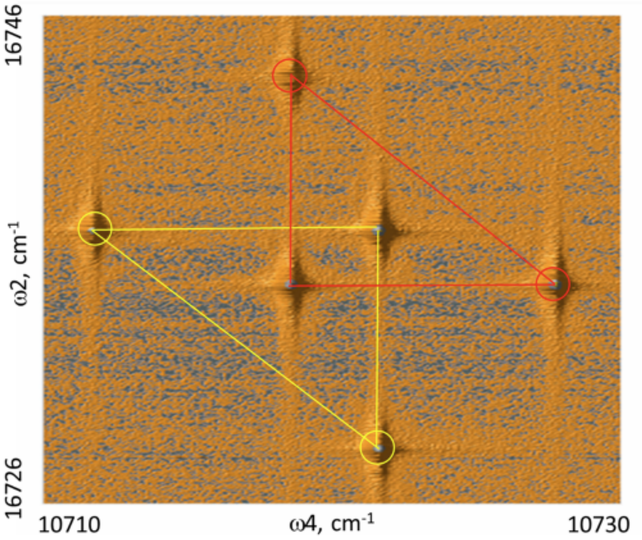

Figure 5. Experimental 2D slice of a HRC3DS spectrum of iodine vapor. The rotational selection rule is $\Delta J = \pm 1$, and the observed basic unit of the rotational pattern is a pair of triangles. This 2D slice shows two different triangles (one yellow and one red), each of which is paired with another triangle (not shown) on a parallel plane. Two of the peaks in the paired triangles have the exact same *x*, *y* coordinates, and those common peaks are circled. The shapes of these triangles and their paired partners were used to identify the FWM process, which is shown in Figure 3D. Adapted with permission from ref 24. Copyright 2018 American Chemical Society.

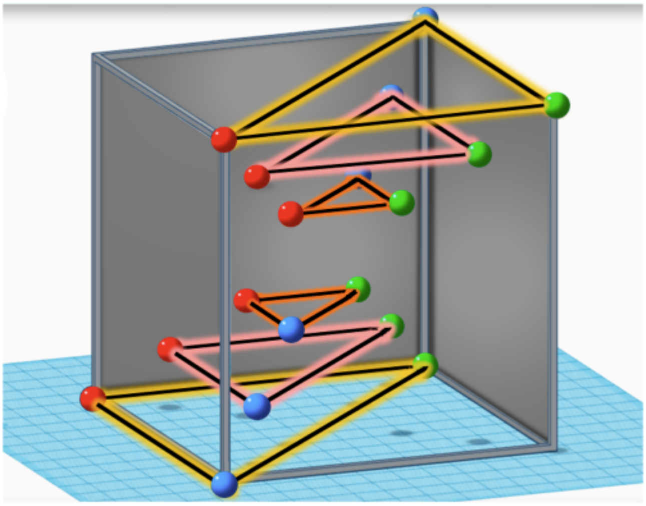

Figure 6. Simplified cartoon of an HRC3DS rotational pattern that is composed of pairs of similarly colored triangles on parallel planes. The two orange triangles are for $J'' = 1$, the pink are for $J'' = 2$, and the yellow are for $J'' = 3$.

peaks for the resulting triangles appearing in the other two (scanned) dimensions have different *x*-axis and *y*-axis coordinates and are therefore resolved in the two other dimensions.

The process of recording and stacking thousands of 2D slices to produce a 3D spectrum is time-consuming and wasteful, given that many of the recorded 2D slices would be void of basic unit peaks due to the low peak density in 3D space. To save time, we have conducted a comprehensive analysis to determine all of the possible FWM processes that can be used to generate HRC3DS spectra based upon a setup that uses two independently tunable dye laser beams and one broadband near-IR beam. Eleven FWM process were identified, and each one produces a unique combination of vibrational patterns, rotational patterns, and output frequency range that can be used to identify it.[2] Of those, the one shown in Figure 3D was identified as the best FWM process for using a time-saving approach where three targeted orthogonal 2D slices through 3D space are acquired in order to find all six peaks needed to form a basic unit. For example, if a scan of $\omega 1$ and $\omega 4$ yields a triangle, then $\omega 1$ should be fixed at the frequency of those peaks while $\omega 2$ and $\omega 4$ are scanned in order to obtain two orthogonal 2D slices that contain the three peaks of the parallel triangle. This approach reduces the time required to record the peaks for a basic rotational unit by 2 to 3 orders of magnitude.[24]

The vibrational and rotational patterns in HRC3DS spectra can be used to identify the FWM process and to calculate the quantum numbers and molecular constants. Figure 7 shows the 3D basic rotational unit that is unique to the FWM processes from Figure 3D. Two different kinds of triangles can be produced, depending upon which two frequencies are scanned to make the 2D slice. Two right triangles (blue and red) can be produced when scanning frequencies $\omega 2$ and $\omega 4$. A pair of acute (round peaks) and obtuse triangles (square peaks) can be produced by scanning frequencies $\omega 1$ and $\omega 4$. Values for the rotational quantum numbers and molecular constants can be extracted from the heights and widths of these triangles. Figure 7 shows these quantitative relationships for a rigid rotor, where the subscripts on the rotational constants correspond to the levels on the FWM diagram. The four measured lengths can be used to set up and solve four independent equations that lead to the rotational quantum number J'' and rotational constants for levels b, c, and d. Multiple basic units produced by different vibrational quantum numbers can lie on the same plane, creating a vibrational pattern in a 2D slice similar to the ones shown in Figure 2 except that the X's are replaced by triangles.[3,22,23] From this vibrational pattern, one can also confirm the FWM process and determine vibrational constants.

■ HIGH-RESOLUTION 2D INFRARED SPECTROSCOPY

Recently, our group has developed an infrared version of HRC2DS that is designed for gas-phase molecules. 2DIR is a well-established form of coherent 2D spectroscopy for condensed-phase samples, but it had not been demonstrated in freely rotating gas molecules until this past year.[4,25] The frequency-based approach that we are using employs doubly resonant vibrationally enhanced (DOVE) techniques[26,27] that were initially developed in the late 1980s and early 1990s[28,29] in John Wright's group at the University of Wisconsin. We call this approach high resolution two-dimensional infrared spectroscopy (HR-2DIR) because higher spectral resolution is needed for gas-phase molecules.

The experimental setup for our HR-2DIR spectrometer involves three separate input beams: a broadband IR, tunable IR, and visible beam. The use of a narrowband visible beam (e.g., at 532 nm) ensures that the output beam wavelengths can be detected with a sensitive CCD. The use of a broadband IR beam allows for rapid multichannel detection. Figure 3E,F shows the two FWM processes called DOVE-IR (Figure 3F) and DOVE-Raman (Figure 3E) that are responsible for generating HR-2DIR peaks.[28]

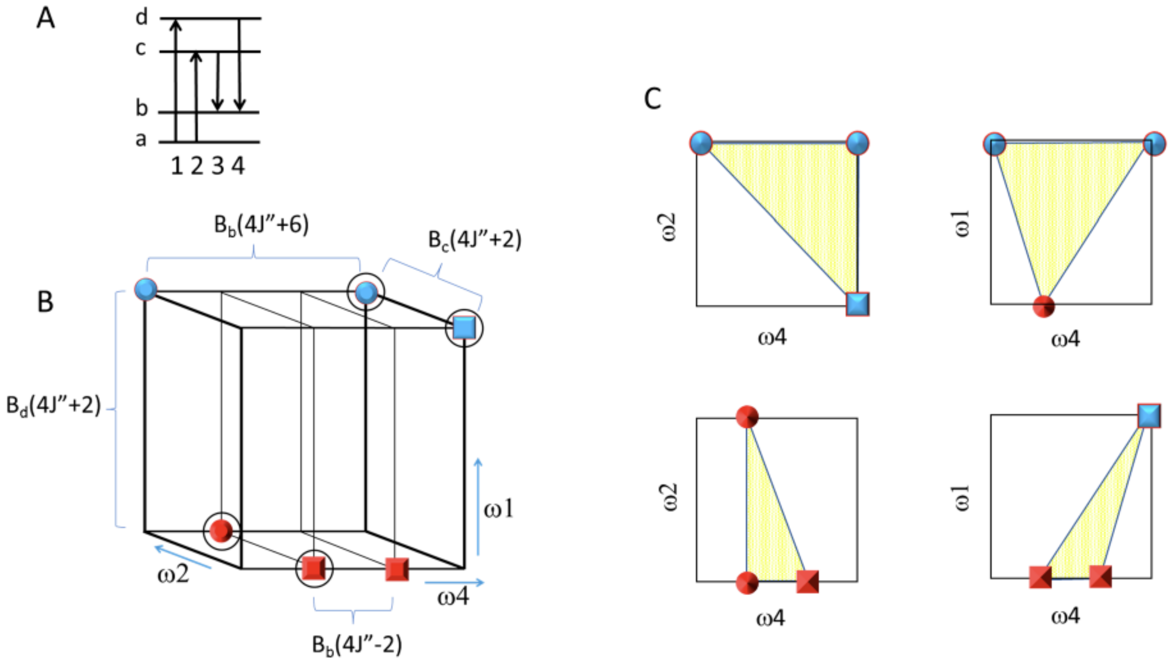

Figure 7. (A) FWM diagram, (B) its 3D rotational basic unit, composed of six peaks that all have the same vibrational and ground-state rotational quantum numbers, and (C) examples of triangles (yellow) produced by targeted orthogonal 2D slices through the 3D rotational basic unit. The three axes $\omega1$, $\omega2$, and $\omega4$ are all tunable frequencies. $\omega3$ is not on any axis because it a broadband near-IR beam. The circled peaks in B have identical x, y coordinates on the $\omega4$, $\omega1$ planes.

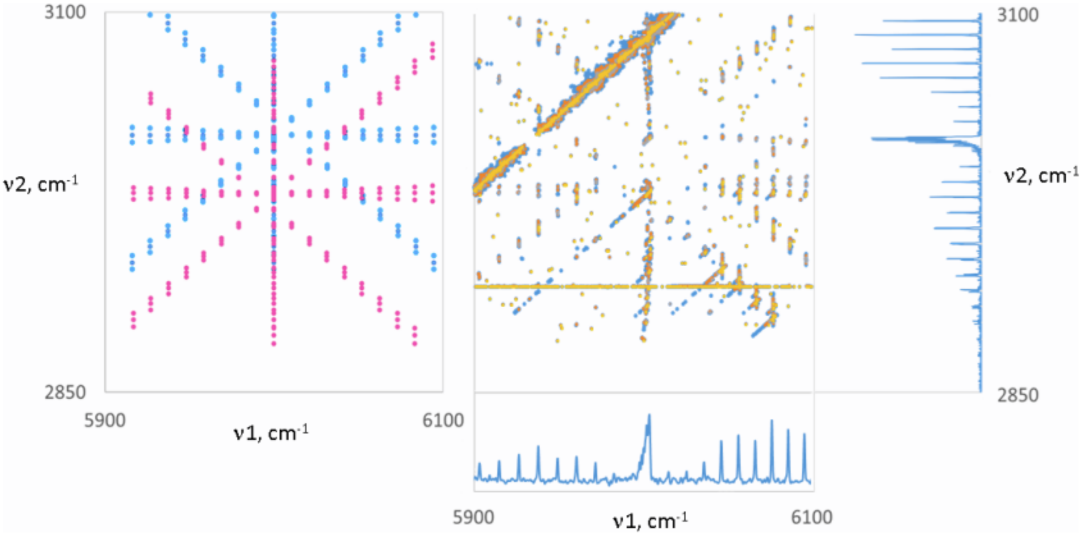

Figure 8. Simulated (left) and experimental (right) HR-2DIR spectra of methane, with IR absorption spectra on the bottom and far right. The pink simulated peaks are from DOVE-Raman (Figure 3E), and the blue simulated peaks are from DOVE-IR (Figure 3F). Extraneous features in the experimental plot such as an intense diagonal line and horizontal line are due to singly resonant FWM processes and a marker used to calibrate the Y axis.

Figure 8 shows a simulated (left) and experimental (right) HR-2DIR spectrum of methane. To record this spectrum, the narrowband IR beam frequency was scanned over methane's CH stretching region while the broadband IR source was set to the CH stretching overtone. The rotational selection rule was $\Delta J = 0, \pm1$, which produces $3 \times 3 = 9$ branches that form an asterisk, one for DOVE-IR and another for DOVE-Raman. The HITRAN database lists >10 000 peaks in this overtone region, most of which are unassigned. However, the 2D peaks that make up the asterisks come only from CH overtone rovibrational peaks that are associated with CH stretching rovibrational peaks. These results indicate that HR-2DIR should be useful for assigning peaks in heavily congested regions of the mid- and near-infrared spectrum.

This proof-of-principle HR-2DIR spectrum is relatively simple because methane is a spherical rotor with just one rotational constant and one rotational quantum number. Other kinds of rotational HR-2DIR patterns should be produced when the technique is applied to other kinds of rotors. For example, symmetric rotors have two rotational quantum numbers (J and K), three rotational constants (A, B, and/or C), and both parallel and perpendicular bands, so their rotational patterns will involve new kinds of patterns. New patterns might also be formed through the coupling of vibrational modes in different regions of the infrared spectrum. Further exploration of different kinds of patterns and their relationships with molecular structure is currently underway with students at Spelman College.

■ CONCLUSIONS, OUTLOOK, AND PERSPECTIVE

Three HRCMDS techniques have been developed that produce spectra containing detailed, informative, and easily recognizable multidimensional patterns, even for systems that yield 1D spectra that appear impossibly congested and patternless. The peaks within rotational and vibrational multidimensional patterns are automatically sorted by species and quantum numbers. A high level of redundancy is useful for determining quantum numbers, molecular constants, and FWM processes, even in the presence of persistent spectral congestion and perturbations. The shapes of the patterns can provide immediate information about selection rules and changes in molecular geometry. Expansion to the third dimension can completely remove spectral congestion and provide selectivity by species, and strategies for reducing acquisition times have been developed.

Earlier work on HRC2DS[1,18−21,30,31] and HRC3DS[2,3,22−24,32] focused on determining how multidimensional patterns from individual molecules can be created and interpreted using electronic resonances. Development of new HRCMDS techniques in the infrared region expands the range of potential applications because infrared techniques are so widely used. New applications could include determining new peak assignments, studying the molecular structure of newly discovered molecules and floppy molecules, and exploring mixtures such as those found in chemical reactions. New improvements in instrumentation, such as the use of frequency combs,[33,34] could further increase the spectral and temporal resolving power of the technique, making it useful for studying larger molecules and dynamics. And to overcome persistent congestion and provide selectivity, future expansion of HR-2DIR into the third dimension is also possible.

Compared to other methods for generating coherent multidimensional spectra, HRCMDS techniques not only are highly effective for studying challenging gas-phase samples but also are relatively simple and inexpensive to set up and operate. All of the work described in this Account was conducted at Spelman College, a small undergraduate institution, a women's college, and an HBCU. Without the resources of a large research university, research groups at predominantly undergraduate institutions (PUIs) work more slowly, but their work can still be significant and groundbreaking. One of the biggest obstacles is the lack of time needed to run experiments and develop creative ideas. PUI faculty usually have heavy teaching responsibilities (e.g., three courses per semester at Spelman College) without help from graduate student teaching assistants. HBCUs also typically do not have endowments or other resources that can help pay for instrumentation purchases, repairs, and support of new or ongoing research. And undergraduate students have less experience and heavier course loads compared to graduate students.

Federal funding has played a major role in helping address these limitations. Title III funding for purchasing laboratory equipment has helped HBCUs purchase much-needed laboratory equipment. My first major research grant in 1996 was through the NASA Faculty Awards for Research program, designated for faculty at minority universities and colleges. And our most recent work on the development of HR-2DIR was funded through the NSF EIR program. These specialized programs can make a huge difference in the research trajectory for faculty at HBCUs. Funding opportunities such as these help to address the large and persistent underrepresentation of minority universities and colleges among the list of awarded grantees funded by large federal research competitions. They give new faculty at HBCUs and PUIs the opportunity to build a productive research program that would otherwise be impossible.

The CHE division of the National Science Foundation has provided essential support needed to carry out the research described in this Account. Some policies such as limiting PI support to 2 months per year were created with research institutions in mind but make it difficult for PUI faculty to maintain active research programs throughout the year. However, some program officers acknowledge the challenges of doing research at a PUI and/or HBCU and encourage inclusion and diversity through flexible policies and practices. For example, in some competitions, proposals from PUIs compete with other PUIs rather than competing with R1 institutions. Building and maintaining a productive research program at an HBCU and/or PUI requires overcoming many obstacles, and encouragement and constructive advice from Lin He, Kelsey Cook, and other NSF CMI program officers have been incredibly helpful.

Finally, I am excited about the opportunity to develop new collaborations that can make use of our new HRCMDS techniques. As a faculty member at an HBCU, I am also aware that not all institutions have a culture that is as deeply dedicated to students from underrepresented groups. My hope is to work with collaborators who genuinely care about supporting the advancement and professional development of our students.

■ AUTHOR INFORMATION

Corresponding Author

Peter C. Chen − *Department of Chemistry and Biochemistry, Spelman College, Atlanta, Georgia 30314, United States;* orcid.org/0000-0001-5481-2635; Email: pchen@spelman.edu

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.accounts.2c00637

Author Contributions

CRediT: **Peter C Chen** conceptualization (lead), funding acquisition (lead), investigation (lead), methodology (lead), writing-original draft (lead).

Notes

The author declares no competing financial interest.

Biography

Peter C. Chen received his A.B. from Cornell University and his Ph.D. from the University of Wisconsin—Madison under the direction of John C. Wright. His research interests are focused on instrumentation and technique development using coherent multidimensional spectroscopy to study gas-phase molecules.

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