Molecular Spectroscopy Workbench

Advances, Applications, and Practical Advice on Modern Spectroscopic Analysis

Emil W. Ciurczak

MOLECULAR SPECTROSCOPY WORKBENCH

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Contributing Editor
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MOLECULAR SPECTROSCOPY WORKBENCH

To Diana, Alex, Adam, Alyssa, and Button and Buster (the Wonder Dogs)

PREFACE

When I first agreed to take over the "Molecular Spectroscopy Workbench" from John Coates, I wasn't sure of the direction or tone that the articles should take. Indeed, to be quite candid, I had no direction for the first few issues. The compass that I came to follow was pointing in the direction I have always taken as a teacher or group leader in industry: explain the technique as if the person listening knew little about it. This works, simply, because a person who has heard it before nods in agreement (feeling comfortable in a review) while a novice appreciates the simple explanation. As the column continued, I made a point of cross-pollination of techniques, attempting to dispense with the esoteric and arcane portions that keep newcomers at bay. I write, in short, for new scientists, students, and practitioners who are interested in hearing about what other spectroscopists, NOT in their particular discipline are doing.

The positive response to "Molecular Spectroscopy Workbench" during the eleven years it has appeared in *Spectroscopy* magazine encouraged me to gather a number of the more interesting articles in one volume. I imagined that the articles might tell an interesting story if put in some logical order. The eight years of columns for which I am responsible have been categorized and arranged in a logical manner (or as logical as the eclectic nature of the column allows) as an anthology. Updates are included whenever information has been "corrected," amended, or I have seen mistakes. Interspersed throughout the anthology are several research papers (either by me or other authors) that also appeared in *Spectroscopy* that fit into this collection. These are complementary to the column articles, as they demonstrate unique applications of vibrational spectroscopy and/or diffuse reflectance behavior.

Since not all possible topics in spectroscopy have been covered in the column in the past seven years, the scope of this anthology does not (and cannot) cover all issues of the art. Rather, a chronology of development may be seen. In fact, several of the chapters are as timely today as they were at printing, several are hopelessly outdated, and most are, to quote Goldilocks, "Just right!" I, myself, was surprised how timely and informative a five- or six-year-old article could still be. Apparently, I chose subjects and guest authors well. The instrument reviews from the various conferences might be seen as a year-by-year

introduction of "state-of-the-art" equipment and when it was first introduced and serve as an historical footnote.

My whole approach to writing the column has always been one of wonder: "I wonder what that word means?" For instance, "What does 'CCD' stand for?" My search of this particular question led to the Hubble Space Telescope, which uses several Charge-Coupled Devices to create images. I had good fortune asking "experts" in the fields where I was a little undereducated. They seemed to like to show off to a humble novice, such as yours truly.

I have tried to mix up my subjects, but, I confess, that I keep coming back to near-infrared spectroscopy (NIRS). I have been playing with NIRS for over 15 years and am still amazed at what it can do. I am equally amazed by the versatility of most instruments in the hands of experienced practitioners. If I seem to have more NIR chapters than any other it may be an inverse rule: There are so many other texts on the other spectroscopic techniques and only three to date on NIRS (1–3).

Perhaps the fact that I am genuinely delighted to learn from the people who help me with columns comes through in the writing. I like to think that my "Oooh-Ahhh!" attitude carries across the page to the reader. I purposely did not date the columns in the body of work, just to show how some have kept their value after half a decade. You may, of course, look at the publication dates in the index, but play along and read the column first. You may be surprised to discover it came out here first!

Since some of the authors have changed jobs, some topics have changed dramatically, or I found "mis-statements" in the text, or there are some small grammatical corrections from the original text. Where a comment will suffice, the italicized words are my editorial comments. Where major rewrites were needed, the new information is likely incorporated into the text. Updates may appear at the end of a particular column . . . what happened subsequent to appearing in the column.

In any case, "Enjoy!" and, hopefully, learn (as did I) something from these pages.

EMIL W. CIURCZAK

Calverton, MD
January, 1997

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First and foremost, I acknowledge the authors of the columns and research papers that I have included: All have taught me something about spectroscopy. To the authors whose names appear on the chapters: Thank you for writing such good articles. To the many people I bothered for information, I also say, "Thank you." You are legion in number, and this book is already long enough, so a general "Thanks" will have to do.

I would like to single out Mike MacRae, once and future editor of *Spectroscopy*. I started with Mike, worked with several other (quite capable) editors, and am back with Mike. He left for a short time and rejoined the *Spectroscopy* family again. He is largely responsible for helping me put this together . . . which is why I won't give out his home address!

My wife, Diana, is the world's greatest proofreader (in addition to being a Ph.D. chemist) . . . she is why MacRae can print my columns without much editing. She usually has helpful hints, such as "Wasn't your column due last week?" and "Didn't you write about that last year?" and the ever-popular, "That doesn't make any sense!" Such are comments that spur me on to greatness, and I love her for it.

My (unpaid) consultants are Howard Mark and Jerome Workman, both also contributing editors for *Spectroscopy*. I have had the pleasure of teaching the ACS Short Course on NIR with both and learned as much as any paying customer. Howie and Jerry keep my observations closer to the "Learning Channel" and away from "X-Files."

And, of course, all the people who read my doggerels and do not demand its removal from *Spectroscopy*. I am always amazed when someone comes up to me at a meeting and admits to being a follower of my scribblings. Thank you, kind people whom I may never meet, save through the printed word. I hope I have done some good and helped with a problem or two. (A smile from one of my bad jokes is appreciated, as well.)

CONTENTS

Preface xv

Acknowledgment xvii

I. Basic Spectroscopic Theory

I. A. Infrared (Midrange)

1. *Echoes of Fundamentals Past or I Don't Think We're Alone in This Spectrum*
   - The comparison of fundamental and overtone absorbances in both the mid-IR and the near-IR. SO_2 is used as a model. **6**(1), 11(1991) / 1
2. *Fourier Transform Spectroscopy: A Dispersive Model*
   - Ron Williams discusses interferometry in terms of dispersive processes and models. **6**(9), 12(1991) / 5

I. B. Infrared (Near)

1. *Near-Infrared Spectroscopy: What it is and What it is Not*
   - Some misconceptions about NIR are discussed. **4**(2), 14(1989) / 13
2. *A Closer Look at the Whole Infrared Region*
   - A comparison of the hardware and working components of spectrometers used in MIR and NIR is given. **7**(3), 12(1992) / 17

I. C. Optical Rotation/Circular Dichroism

1. *Chiroptic Phenomena, Part I: Circular Birefringence—Optical Rotation and Optical Rotatory Dispersion*
   - Harry G. Brittain discusses the theory behind ORD using math and words to illustrate his points. **6**(3), 11(1991) / 21
2. *Chioptic Phenomena, Part II: Circular Dichroism*
   - Harry G. Brittain demonstrates equipment, theory, and applications of CD in this second part of his article. **6**(6), 13(1991) / 27

3. *Monitoring Conformational Transitions in Synthetic DNA Oligomers Using Circular Dichroism*
   - Richard D. Sheardy explains his work with DNA, using the tool of CD to aid in his conformational studies. **6**(7), 14(1991) / 33

II. Applied Spectroscopy

II. A. Infrared (Midrange)

1. *Near-Infrared Analysis at DuPont: Historical Perspective*
   - Eugene S. Taylor talks about the evolution of IR and NIR at DuPont, beginning in 1952. A general historic overview. **4**(7), 10(1989) / 43
2. *Infrared Sample Preparation, or, It's Not the Same Old Grind*
   - Various sample presentation techniques are discussed, along with applications and potential problems and solutions. **9**(6), 18(1994) / 49
3. *Culinary Spectroscopy—FT-IR Analysis of Cooking and Cuisine*
   - Gerald J. (Dr. Demento) DeMenna shows that IR does belong in the kitchen. He gives cooking tips and information on the chemistry of food preparation using modern techniques. **4**(3), 10(1989) / 55
4. *Happiness Is a Warm Sample*
   - Photoacoustic spectrometry is discussed, and some examples of its use are given. **10**(2), 16(1995) / 65
5. *Nonstandard Spectroscopic Measurements (or, What To Do When It's Not a Clear Solution or Filter . . .)*
   - Arthur Springsteen gives the low-down on the physics of integrating spheres used in the infrared (and UV/vis/NIR). **12**(4), 24(1997) / 69

II. B. Infrared (Near)

1. *Part 1: Arterial Analysis with a Novel Near-IR Fiber-Optic Probe. Part 2: Instrument Repair Survey Results*
   - Rob Lodder and Lisa Cassis discuss the application of NIR to the determination of LDL and HDL on arterial walls nonintrusively. **5**(7), 12(1990) / 79
2. *Identification of Actives in Multicomponent Pharmaceutical Dosage Forms Using Near-Infrared Reflectance Analysis*
   - Ciurczak and Thomas A. Maldacker use three different algorithms and approaches to identify the active drug and approximate the amount of the same. This work predates principal components analysis and uses early matrix algebra algorithms. A comment by Donald A. Burns follows. **1**(1), 36(1986) / 89

3. *Evaluation of a Near-Infrared Detector for High-Performance Liquid Chromatography*
   - Ciurczak and Frances M. B. Weis discuss the first design and preliminary results of an NIR-HPLC detector. This is the work that became my doctoral thesis. **2**(10), 33(1987) / 99

4. *Parameters of a Near-IR HPLC Detector, Part I: Limits of Analytical Sensitivity for Reversed-Phase Chromatographic Systems*
   - Emil W. Ciurczak and Tracey A. Dickinson discuss the application of NIR to water-based chromatographic systems; quantitation is stressed. **6**(2), 12(1991) / 111

5. *Parameters of a Near-IR HPLC Detector, Part II: Application to NonAqueous Systems*
   - Emil W. Ciurczak, T. Dickinson, and W. R. Murphy discuss non-water-based chromatography from analytical to preparative levels in concentration. Both qualitative and quantitative applications of the detector are discussed. **6**(8), 13(1991) / 119

6. *The Design Parameters of a Near-Infrared Detector for High-Performance Liquid Chromatography*
   - Emil W. Ciurczak and Ina M. Vance discuss the possible mechanical and electronic components for a detector used in absorbance and derivative NIR-HPLC work. **3**(9), 56(1988) / 127

7. *Determination of Enantiomeric Purity of Valine via Near-Infrared Reflectance Spectroscopy*
   - Emil W. Ciurczak, Bruce R. Buchanan, Art Q. Grunke, and David E. Honigs use NIR to determine ratio of D- and I-valine isomers in dry, crystalline racemic mixtures. **3**(5), 54(1988) / 135

8. *Analysis of Solid and Liquid Dosage Forms Using Near-Infrared Reflectance Spectroscopy*
   - Emil W. Ciurczak and Ronald P. Torlini discuss application of NIR to multicomponent solid and liquid dosage forms. **2**(3), 41(1987) / 143

9. *Determination of Particle Size of Pharmaceutical Raw Materials Using Near-Infrared Reflectance Spectroscopy*
   - Emil W. Ciurczak, Ronald P. Torlini, and Michael P. Demkowicz show how diffusely reflected NIR spectra may be used to estimate the mean particle size of the powders tested. **1**(7), 36(1986) / 151

10. *Applications of Near-IR Spectroscopy in the Pharmaceutical Industry*
    - Emil W. Ciurczak and Jim Drennen take a look at the latest NIR research in this important industry. **7**(6), 12(1992) / 159

II. C. UV/Vis and Fluorescence

1. *Chemometrics: A Powerful Toolbox for UV/vis Spectroscopy*
   - Jerry Workman explains, in simple terms, the application of powerful mathematical algorithms to UV/vis. **4**(6), 10(1989) / 165
2. *A Real "Cool" Technique and Other Musings*
   - Low temperature fluorescence hardware and theory is discussed. Divergence of light from dipping fiber optic probes is also discussed as well as potential problems associated with them.
     10(7), 18(1995) / 173
3. *To Describe in Glowing Terms*
   - More fluorescence and phosphorescence applications/theory.
     10(3), 14(1995) / 177
4. *File Transfer Software for UV/vis Spectroscopy—An OS/2-Based Program for Dynamic Data Exchange*
   - John Sanders provides a program suitable for today's and older instruments. **11**(6), 24(1996) / 181

II. D. Mass Spectrometry

1. *Getting a Charge out of Mass Spectrometry*
   - Kenneth Busch describes various methods of ionization in MS.
     9(4), 12(1994) / 191
2. *Photon Resonance Mass Spectrometry*
   - John Wronka describes technique using a tunable IR laser to desorb macromolecules selectively. **5**(3), 10(1990) / 197

II. E. Acousto-Optic Tunable Filters

1. *A Novel Spectrophotometer System Based on an Acousto-Optical Tunable Filter*
   - Theory and operations parameters of a commercial AOTF instrument. Strengths and weaknesses are discussed.
     5(1), 10(1990) / 203
2. *An AOTF-Illuminated Microscope*
   - Work performed by NIH with a Brimrose-manufactured AOTF microscope is described. Wavelengths range from UV to far-IR.
     8(2), 12(1993) / 207

II. F. Fiber Optics

1. *Shedding Light on Fiber Optics*
   - A primer of an article by Scott Wohlstein about the basic theories and some applications of fiber-optic materials.
     8(5), 12(1993) / 211

2. *Fiber-Optic Multiplexers*
   - Bruce Buchanan and Patrick O'Rourke describe the automated fiber-optic multiplexer system developed at Savannah River, GA, for IR and NIR multistation monitoring of some nasty materials.
   9(3), 12(1994) / 215

II. G. Miscellaneous Techniques/New Hardware

1. *What is FT-Raman, and Where Can I Use it?*
   - Mary Ann Finch gives a succinct explanation of the theory, hardware, and some applications of FT-Raman.
   5(6), 12(1990) / 221
2. *A Commercial Near-IR Diode-Array Spectrophotometer*
   - The theory of diode arrays for NIR as well as two manufacturers' equipment are described herein. **7**(9), 12(1992) / 233
3. *An LED-Based, Near-IR Process Spectrometer*
   - The Katrina, short-wavelength instrument, based on sequentially firing diodes, is described. **8**(1), 14(1993) / 237
4. *Pictures from Numbers and the Littlest Spectrometer*
   - The theory and application of CCDs (charge-coupled devices) are discussed; the Hubble Space Telescope is used as one example, HPLC detectors are examined as spectrometers.
   10(1), 14(1995) / 241
5. *Hadamard Transform Spectroscopy: Teaching Old Monochromators New Tricks*
   - Robert M. Hammaker, William G. Fateley, and David C. Tilotta discuss the first commercial Hadamard instrument. Extensive theory and mathematics are included. [As a further reference, see "Hadamard Transform Infrared Spectroscopy," Z. Zhou and D. C. Tilotta, *Spectroscopy*, **6**(8), 26(1991).] **3**(1), 14(1988) / 245
6. *Lasers: The Quantum Monkey Wrench*
   - Scott Wohlstein discusses the types and parameters of commercially available and experimental lasers. **4**(9), 10(1989) / 263
7. *Detectors in Infrared Spectroscopy*
   - First in the series of four chapters. The various types of detectors for near-, mid-, and far-range infrared instrumentation are described and discussed. Designed as a primer.
   8(9), 12(1993) / 273
8. *Common Sources and Signal Processing Techniques Used in Vibrational Spectroscopy*
   - Second in a series of four chapters. A listing of all potential light sources used in IR/NIR. Designed as a primer.
   8(10), 12(1993) / 277

9. *Monochromators Used in Vibrational Spectroscopy*
   - Third in a series of four chapters. A description of various types of monochromators (dispersive and nondispersive) used in vibrational spectroscopy. Designed as a primer.

   9(1), 12(1994) / 287

10. *Building the Perfect Spectrometer or Pick One from Column A and One from Column B . . .*
   - Last in a series of four related chapters: Tying the previous three chapters (sources, monochromators, and detectors) together in a "how-to" guide for analysts. Designed as a primer.

   9(2), 12(1994) / 293

11. *Taking the Spectroscopy of Fluids beyond the Limits*
   - Valentine J. Rossiter discusses spectroscopy cell used at the extremes of pressure and temperature. **10**(6), 18(1995) / 299

12. *More Perspectives on the Decade in Spectroscopy*
   - Claudio Puebla tells about the updates in software since *Spectroscopy* first started publishing in "Ten Years of Computational Chemistry." Near-field scanning optical microscopy is discussed by Dan Higgins. In "Once again into the Fray," Ciurczak discusses how to select the number of samples for calibration of an on-line instrument. **11**(1), 24(1996) / 307

III. General Troubleshooting

1. *Purgamenta Iniunt, Purgamenta Exiunt*
   - A look at the folly of trying to correct poor spectra with the power of computers. *Caveat emptor* is the key. (A "Latin" flavor!). **7**(1), 12(1992) / 315

2. *A Look at Validation for Spectroscopic Instrumentation: The FDA Has Taken the Lead*
   - The concepts behind the need and procedures used in validation. The definition of "validation" is examined.

   8(7), 12(1993) / 319

3. *Chemical Intuition in Analytical Testing: A Case Study*
   - Elisa Lyth and Lily M. Ng show how a little forensics thinking in everyday lab work helped solve a problem. An unknown peak led to an understanding of a problem. **9**(5), 12(1994) / 325

4. *Two Valuable Tools for Instrument Evaluation: JCAMP.DX and Price Tags*
   - A new standard file structure, similar to ASCII and the cost/value relationship of new instruments are discussed.

   4(8), 12(1989) / 331

5. *Nobody Knows the Troubles I've Seen . . .*
   • Several instrumentation problems solved. Moisture on IR windows, alcohol used to stabilize alkenes and alkynes.
   9(8), 22(1994) / 335
6. *Some More Uh-Ohs for the Vibrational Spectroscopist*
   • Assorted troubleshooting tips: dying lamps, stray light, fiber-optics, diagnostics for mulls, thin films, and KBr pellets.
   9(9), 28(1994) / 339
7. *Learning Tools: Chemistry Education and Molecular Modeling*
   • The curricula in secondary schools as well as college and graduate teaching methodology are discussed. Molecular modeling as a tool is looked at along with several programs available.
   8(3), 12(1993) / 343
8. *What's in a Name? And Reflections on a Dusty Surface*
   • More troubleshooting tips on cleaning cuvettes, etc.
   9(7), 16(1994) / 349
9. *Questions and Answers on Process Analysis: Tips for Selecting and Calibrating IR Instruments*
   • Some questions arising from the ACS Short Course on NIR, but applied to IR as well. **10**(9), 18(1995) / 353

IV. Review Columns

IV. A. Conferences

1. *A Review of the Third International Conference on Near-Infrared Spectroscopy*
   • Program highlights and details on nonagricultural papers presented in Brussels in June, 1990. **5**(8), 14(1990) / 357
2. *"What's New in Spectroscopy?" A Report on PittCon '92 in New Orleans*
   • Notable UV/vis/near-IR papers given at PittCon 1992.
   7(4), 16(1992) / 361
3. *A Report from the Sixth International Diffuse Reflectance Conference*
   • A review of the technical program from Chambersburg, PA, on the 1992 biennial conference. **7**(8), 12(1992) / 363
4. *"What's New in Spectroscopy?" PittCon '93 in Atlanta*
   • Scope of discussion and important papers presented at the annual conference in 1993. **8**(4), 16(1993) / 367
5. *Near-Infrared Topics from the 1994 PittCon*
   • Important topics discussed in 1994. **9**(4), 29(1994) / 369
6. *Near-Infrared Topics from the 1995 PittCon*
   • Important topics discussed in 1995. **10**(5), 42(1995) / 371

7. *The Good Old Days, or What?*
   - Musings on the last 10 years for the anniversary issue.
   10(8), 22(1995) / 373
8. *Review of the 8th International Diffuse Reflectance Conference (1996): or "Round Up the Usual Suspects!"*
   - The Chambersburg meeting is reviewed for content and impact.
   12(2), 15(1997) / 377

IV. B. New Equipment and Miscellaneous
1. *A New Beginning and a Wrapup of What's New in Instrumentation*
   - A review of new instruments since PittCon 1988 and the first column written by Ciurczak. **4**(1), 18(1989) / 381
2. *Pittsburgh Conference Review: 1989 in Atlanta*
   - A review of spectroscopic hardware, software, and accessories at the Pittsburgh Conference. **4**(4), 10(1989) / 389
3. *Instrument Service Survey*
   - A call to users for instrument maintenance info.
   5(2), 12(1990) / 409
4. *1990 PittCon Product Wrapup, Part 1: Instrumentation for Molecular Spectroscopy*
   - Instruments, software, and accessories for spectroscopic work, listed by increasing wavelength. **5**(4), 12(1990) / 413
5. *"What's New in Spectroscopy Instrumentation?" 1991 PittCon Wrapup*
   - Last review done on ALL equipment from UV-vis through far-IR, MS, NMR, etc. **6**(4), 12(1991) / 433
6. *Internet Sites for Infrared and Near-Infrared Spectrometry, Part I: Online Instruction and Direct Communication*
   - Rob Lodder and Elizabeth G. Kraemer present a list of Web sites and newsgroups for the IR community as well as some commentary of the future impact of electronic media on scientific education and publishing. **11**(7), 24(1996) / 451
7. *Internet Sites for Infrared and Near-Infrared Spectrometry, Part II: Promotional Sites and Online Publications*
   - The second part of the listing of Web sites compiled by Rob Lodder and Elizabeth G. Kraemer, focusing on promotional sites and online publications. **11**(8), 17(1996) / 461

CHAPTER I.A.1

ECHOES OF FUNDAMENTALS PAST OR I DON'T THINK WE'RE ALONE IN THIS SPECTRUM

This column is an answer to all those criticisms about near-infrared that begin, "But it's only overtones and combinations . . ." I wrote this in attempt to show those "real" *spectroscopists that they have been using overtones and combination bands for years without thinking. Not only that, but chose to open the anthology with one of my favorites.*

My subject this month is one near and dear to my heart: overtones and combinations in vibrational spectroscopy. While these are the heart of near-infrared (near-IR), they are quite common in midrange IR as well. The example I am using to illustrate overtones and combinations is the simple gas SO_2. (1)

From the common, everyday formula for vibrational modes (number of modes = $3N - 6$), it is expected that gaseous SO_2 would have three bands in the IR region. The first vibration (*I used calculations based on the vibrational "Hooke's Law" approach, which matches quite well with higher-level quantum-mechanical calculations, well beyond my simple calculator.*) is ν_1, the *symmetric stretch* (Fig. 1a), and it gives a peak at 1151 cm^{-1}. (This can be calculated by group theory, or you can take my word for it!) A second stretch ν_3 is called the *asymmetric stretch* (Fig. 1b) and has a frequency of 1361 cm^{-1}, or slightly more energy than the first. A third absorbance at 519 cm^{-1}, ν_2, comes from the O–S–O bending and is called (cleverly enough) the *bending mode* (Fig. 1c). (Note: The numbering of these bands is consistent with conventions that cannot be explained in a column of this length.)

The above assignment of vibrational modes would be a perfect example of