Preface to the 3rd edition

The new edition of *Organic Synthesis* has been revised and rewritten from front to back. I want to thank all who used the book in its first and second editions. The book has been out of print for several years, but the collaboration of Warren Hehre and Wavefunction, Inc. made the third edition possible. It is the same graduate level textbook past users are familiar with, with two major exceptions. First, the book has been revised and updated. Second, molecular modeling problems are included in a manner that is not obtrusive to the theme of understanding reactions and synthesis. More than 60 molecular modeling problems are incorporated into various discussions, spread throughout 11 of the 13 reactions-synthesis oriented chapters. These are intended for the *SpartanModel* program, a copy of which is included in the purchase price of this book. *SpartanModel* will allow the reader to manipulate each model and, in most cases, change or create model compounds of interest to the reader. It is our belief that the selected molecular modeling problems will offer new insights into certain aspects of chemical reactivity, conformational analysis, and stereoselectivity.

Updated examples are used throughout the new edition when possible, and new material is added that make this edition reflect current synthetic methodology. The text has been modified in countless places to improve readability and pedagogy. This new edition contains references taken from more than 6100 journal articles, books, and monographs. Of these references, more than 950 are new to this edition, all taken from the literature after 2002. More than 600 updated or new reactions have been added. There are several entirely new sections that discuss topics missing from the 2nd edition. These include S_N2 type reactions with epoxides; the Burgess Reagent; functional group rearrangements (Beckmann, Schmidt, Curtius, Hofmann, Lossen); Oxidation of allylic carbon with ruthenium compounds; A comparison of LUMO-mapping with the Cram model and Felkin-Anh models in chapter 4; Electrocyclic reactions; [2,3]-sigmatropic rearrangement (Wittig rearrangement); consolidation of C–C bond forming reactions of carbocations and nucleophiles into a new section.

Homework in each chapter has been extensively revised. There are more than 800 homework problems, and more than 300 of the homework problems are new. Most of the homework problems do not contain leading references for the answers. The answers to all problems from chapters 1-9, and 11-13 are available in an on-line *Student Solutions Manual* for this book. As in previous edition, a few leading references are provided for the synthesis problems in chapter 10. Although answers are given for homework that relates to all other chapters, in chapter 10 most problems do not have answers. The student is encouraged to discuss any synthetic problem with their instructor.
With the exception of scanned figures, all drawings in this book were prepared using ChemDraw, provided by CambridgeSoft, and all 3D graphics are rendered with Spartan, provided by Wavefunction, Inc. I thank both organizations for providing the software that made this project possible.

I express my gratitude to all of those who were kind enough to go through the first and second editions and supply me with comments, corrections, and suggestions.

For this new edition, special thanks and gratitude are given to Warren Hehre. Not only did he design the molecular modeling problems, but provided the solutions to the problems and the accompanying software. Warren also helped me think about certain aspects of organic synthesis in a different way because of the modeling, and I believe this has greatly improved the book and the approaches presented in the book. Special thanks are also given to Ms. Pamela Ohsan, who converted the entire book into publishable form. Without her extraordinary efforts, this third edition would not be possible.

Finally, I thank my students, who have provided the inspiration over the years for this book. They have also been my best sounding board, allowing me to test new ideas and organize the text as it now appears. I thank my friends and colleagues who have provided countless suggestions and encouragement over the years, particularly Spencer Knapp (Rutgers), George Majetich (Georgia), Frederick Luzzio (Louisville), and Phil Garner (Washington State). You have all helped more than you can possibly know, and I am most grateful.

A special thanks to my wife Sarah and son Steven, whose patience and understanding made the work possible.

If there are errors, corrections, and suggestions, please let me know by Email or normal post. Any errors will be posted at http://books.wavefun.com/organicsynthesis3rd.

Thank you again. I hope this new edition is useful to you in your studies.

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Preface to the 1st edition. Why I wrote this book!

A reactions oriented course is a staple of most graduate organic programs, and synthesis is taught either as a part of that course or as a special topic. Ideally, the incoming student is an organic major, who has a good working knowledge of basic reactions, stereochemistry and conformational principles. In fact, however, many (often most) of the students in a first year graduate level organic course have deficiencies in their undergraduate work, are not organic majors and are not synthetically inclined. Does one simply tell the student to “go away and read about it,” giving a list of references, or does one take class time to fill in the deficits? The first option works well for highly motivated students with a good background, less well for those with a modest background. In many cases, the students spend so much time catching up that it is difficult to focus them on the cutting edge material we all want to teach. If one exercises the second option of filling in all the deficits, one never gets to the cutting edge material. This is especially punishing to the outstanding students and to the organic majors. A compromise would provide the student with a reliable and readily available source for background material that could be used as needed. The instructor could then feel comfortable that the proper foundations have been laid and push on to more interesting areas of organic chemistry.

Unfortunately, such a source of background material either is lacking altogether or consists of several books and dozens of review articles. I believe my teaching experience at UConn as just described is rather typical, with a mix of non-organic majors, outstanding and well-motivated students, and many students with weak backgrounds who have the potential to go on to useful and productive careers if time is taken to help them. Over the years I have assigned what books were available in an attempt to address these problems, but found that “graduate level textbooks” left much to be desired. I assembled a large reading list and mountains of handouts and spent half of my life making up problems that would give my students a reasonable chance at practicing the principles we were discussing. I came to the conclusion that a single textbook was needed that would give me the flexibility I craved to present the course I wanted to teach, but yet would give the students the background they needed to succeed. As I tried different things in the classroom, I solicited the opinions of the graduate students who took the course and tried to develop an approach that worked for them and allowed me to present the information I wanted. The result is this book. I hope that it is readable, provides background information, and also provides the research oriented information that is important for graduate organic students. I also hope it will be of benefit to instructors who face the same challenges I do. I hope this book will be a useful tool to the synthetic community and to graduate level education.

From talks with many people I know that courses for which this book is targeted can be for either one or two semesters. The course can focus only on functional groups, only on making carbon-carbon bonds, on some combination of both (like my course), or only on synthesis.
I have tried to organize the book in such a way that one is not a slave to its organization. Every chapter is internally cross-referenced. If the course is to focus upon making carbon-carbon bonds, for example, there are unavoidable references to oxidation reagents, reducing agents, stereochemical principles, etc. When such a reaction or principle appears, the section and chapter where it is discussed elsewhere in the book is given “in line” so the student can easily find it. It is impossible to write each chapter so it will stand alone, but the chapters are reasonably independent in their presentations. I have organized the book so that functional groups are discussed in the first few chapters and carbon-carbon bond formation reactions are discussed in later chapters, making it easier to use the one book for two different courses or for a combination course. The middle chapters are used for review and to help the student make the transitions from functional group manipulations to applying reactions and principles and thence to actually building molecules. I believe that a course devoted to making carbon-carbon bonds could begin with chapter 8, knowing that all pertinent peripheral material is in the book and readily available to the student. The ultimate goal of the book is to cut down on the mountains of handouts, provide homework to give the student proper practice, give many literature citations to tell the student exactly where to find more information, and allow the instructor to devote time to their particular focus.

This book obviously encompasses a wide range of organic chemistry. Is there a theme? Should there be? The beautiful and elegant total syntheses of interesting and important molecules published by synthetic organic chemists inspired me to become an organic chemist, and I believe that synthesis focuses attention on the problems of organic chemistry in a unique way. To solve a synthetic problem, all elements of organic chemistry must be brought to bear: reactions, mechanism, stereochemistry, conformational control, and strategy. Synthesis therefore brings a perspective on all aspects of organic chemistry and provides a theme for understanding it. The theme of this book is therefore the presentation of reactions in the context of organic synthesis. Wherever possible, examples of a given reaction, process, or strategy are taken from a published total synthesis. The disconnection approach is presented in the first chapter, and as each new functional group transform and carbon-carbon bond forming reaction is discussed, the retrosynthetic analysis (the disconnect products for that reaction) is given. An entire chapter (chapter 10) is devoted to synthetic strategies, and chapter 14 provides examples of first year students’ first syntheses. I believe that this theme is a reasonable and useful device for presenting advanced organic chemistry.

The text is fully referenced to facilitate further study, and (where feasible) the principal researcher who did the work is mentioned by name, so the student can follow that person’s work in the literature and gain even more insight into a given area. As far as it is known to me, the pioneering work of the great chemists of the past has been referenced. Many of the “named reactions” are no longer referenced in journals, but when they are first mentioned in this book, the original references are given. I believe the early work should not be lost to a new generation of students.
In many cases I have used 3-D drawings to help illustrate stereochemical arguments for a given process. I give the structure of each reagent cited in the text, where that reagent is mentioned, so a beginning student does not have to stop and figure it out. This is probably unnecessary for many students, but it is there if needed.

This is a reaction oriented book, but an attempt is made to give brief mechanistic discussions when appropriate. In addition, some physical organic chemistry is included to try to answer the obvious if unasked questions: why does that alkyl group move, why does that bond break, why is that steric interaction greater than the other one, or why is that reaction diastereoselective?

Most of all, a student needs to practice. Chapters 1-13 have end-of chapter problems that range from those requiring simple answers based on statements within the text to complex problems taken from research literature. In a large number of cases literature citations are provided so answers can be found.

The first part of the book (chapters 1-4) is a review of functional group transforms and basic principles: retrosynthesis, stereochemistry, and conformations. Basic organic reactions are covered, including substitution reactions, addition reactions, elimination reactions, acid/base chemistry, oxidation and reduction. The first two chapters are very loosely organized along the lines of an undergraduate book for presenting the functional group reactions (basic principles, substitution, elimination, addition, acyl addition, aromatic chemistry). Chapter 1 begins with the disconnection approach. I have found that this focuses the students’ attention on which reactions they can actually apply and instantly shows them why it is important to have a larger arsenal of reactions to solve a synthetic problem. This has been better than any other device I have tried and that is why it is placed first. Most of the students I see come into our program deficient in their understanding of stereochemistry and conformational control, and so those topics are presented next. Some of this information is remedial material and where unneeded can be skipped, but it is there for those who need it (even if they will not admit that they do). Chapter 2 presents a mini-review of undergraduate organic chemistry reactions and also introduces some modern reactions and applications. Chapter 3 is on oxidation and chapter 4 is on reduction. Each chapter covers areas that are woefully under-emphasized in undergraduate textbooks.

Chapter 5 covers hydroboration, an area that is discussed in several books and reviews. I thought it useful to combine this material into a tightly focused presentation which (1) introduces several novel functional group transforms that appear nowhere else and (2) gives a useful review of many topics introduced in chapters 1-4. Chapter 6 reviews the basic principles that chemists use to control a reaction rather than be controlled by it. It shows the techniques chemists use to “fix” the stereochemistry, if possible, when the reaction does not do what it is supposed to. It shows how stereochemical principles guide a synthesis. An alternative would be to separate stereochemistry into a chapter that discusses all stereochemical principles. However, the theme is synthesis, and stereochemical considerations are as important a part of a synthesis as the reagents being chosen. For that reason, stereochemistry is presented with the reactions
in each chapter. Chapter 6 simply ties together the basic principles. This chapter also includes the basics of ring-forming reactions. Chapter 7 completes the first part of the book and gives a brief overview of what protecting groups are and when to use them.

The last half of the book focuses on making carbon-carbon bonds. It is organized fundamentally by the disconnection approach. In Chapter 1, breaking a carbon-carbon bond generated a disconnect product that was labeled as \(C^d\) (a nucleophilic species), \(C^n\) (an electrophilic species), or \(C^{\text{radical}}\) (a radical intermediate). In some cases, multiple bonds were disconnected, and many of these disconnections involved pericyclic reactions to reassemble the target. The nucleophilic regents that are equivalent to \(C^d\) disconnect products are covered in Chapters 8 and 9, with the very important enolate anion chemistry separated into Chapter 9. Chapter 10 presents various synthetic strategies that a student may apply to a given synthetic problem. This information needs to be introduced as soon as possible, but until the student “knows some chemistry”, it cannot really be applied. Placement of synthetic strategies after functional group transforms and nucleophilic methods for making carbon-carbon bonds is a reasonable compromise. Chapter 11 introduces the important Diels-Alder cyclization, as well as dipolar cycloadditions and sigmatropic rearrangements that are critically important to synthesis. Chapter 12 explores electrophilic carbons (\(C^n\)), including organometallics that generally react with nucleophilic species. Chapter 13 introduces radical and carbene chemistry. Chapter 14 is included to give the student a taste of a first time student proposal and some of the common mistakes. The point is not to reiterate the chemistry but to show how strategic shortsightedness, poor drawings, and deficiencies in overall presentation can influence how the proposal is viewed. It is mainly intended to show some common mistakes and also some good things to do in presenting a synthesis. It is not meant to supersede the detailed discussions of how and why a completed elegant synthesis is done but to assist the first-time student in preparing a proposal.

The goal of this work is to produce a graduate level textbook, and it does not assume that a student should already know the information, before the course. I hope that it will be useful to students and to the synthetic community. Every effort has been made to keep the manuscript error-free. Where there are errors, I take full responsibility and encourage those who find them to contact me directly, at the address given below, with corrections. Suggestions for improving the text, including additions and general comments about the book are also welcome. My goal is to incorporate such changes in future editions of this work. If anyone wishes to contribute homework problems to future editions, please send them to me and I will, of course, give full credit for any I use.

I must begin my “thank yous” with the graduate students at UConn, who inspired this work and worked with me through several years to develop the pedagogy of the text. I must also thank Dr. Chris Lipinski and Dr. David Burnett of Pfizer Central Research (Groton, CT) who organized a reactions/synthesis course for their research assistants. This allowed me to test this book upon an “outside” and highly trained audience. I am indebted to them for their
There are many other people to thank. Professor Janet Carlson (Macalester College) reviewed a primeval version of this book and made many useful comments. Professors Al Sneden and Suzanne Ruder (Virginia Commonwealth University) classroom tested an early version of this text and both made many comments and suggestions that assisted me in putting together the final form of this book. Of the early reviewers of this book, I would particularly like to thank Professor Brad Mundy (Colby College) and Professor Marye Anne Fox (University of Texas, Austin), who made insightful and highly useful suggestions that were important for shaping the focus of the book.

Along the way, many people have helped me with portions or sections of the book. Professor Barry Sharpless (Scripps) reviewed the oxidation chapter and also provided many useful insights into his asymmetric epoxidation procedures. Dr. Peter Wuts (Upjohn) was kind enough to review the protecting group chapter (chapter 7) and helped me focus it in the proper way. Professor Ken Houk (UCLA), Professor Stephen Hanessian (Université de Montréal), Professor Larry Weiler (U. of British Columbia), Professor James Hendrickson (Brandeis), Professor Tomas Hudlicky (U. Florida), and Professor Michael Taschner (U. of Akron) reviewed portions of work that applied to their areas of research and I am grateful for their help.

Several people provided original copies of figures or useful reprints or comments. These include Professor Dieter Seebach (ETH), Professor Paul Williard (Brown), Professor E.J. Corey (Harvard), Dr. Frank Urban (Pfizer Central Research), Professor Rene Barone (Université de Marseilles), and Professor Wilhelm Meier (Essen).

Two professors reviewed portions of the final manuscript and not only pointed out errors but made enormously helpful suggestions that were important for completing the book: Professor Fred Ziegler (Yale) and Professor Douglass Taber (U. of Delaware). I thank both of them very much.

There were many other people who reviewed portions of the book and their reviews were very important in shaping my own perception of the book, what was needed and what needed to be changed. These include: Professor Winfield M. Baldwin, Jr. (U. of Georgia), Professor Albert W. Burgstahler (U. of Kansas), Professor George B. Clemens (Bowling Green State University), Professor Ishan Erden (San Francisco State University), Professor Raymond C. Fort, Jr. (U. of Maine), Professor John F. Helling (U. of Florida), Professor R. Daniel Little (U. of California), Professor Gary W. Morrow (U. of Dayton), Professor Michael Rathke (Michigan State University), Professor Bryan W. Roberts (U. of Pennsylvania), Professor James E. Van Verth (Canisius College), Professor Frederick G. West (U. of Utah), and Professor Kang Zhao (New York University). I thank all of them.

I must also thank the many people who have indulged me at meetings, at Gordon conferences, and as visitors to UConn and who discussed their thoughts, needs, and wants in graduate level
education. These discussions helped shape the way I put the book together.

Finally, but by no means last in my thoughts, I am indebted to Professors Joe Wolinsky and Jim Brewster of Purdue University. Their dedication and skill taught me how to teach. Thank you!

I particularly want to thank my wife Sarah and son Steven. They endured the many days and nights of my being in the library and the endless hours on the computer with patience and understanding. My family provided the love, the help, and the fulfillment required for me to keep going and helped me to put this project into its proper perspective. They helped me in ways that are too numerous to mention. I thank them and I dedicate this work to them.

Michael B. Smith
Introducing SpartanModel

*SpartanModel* is an virtual model kit, designed to provide students of organic chemistry information about molecular structure, stability and properties. In the simplest of terms, *SpartanModel* is the 21st century equivalent of “plastic models” used by students of previous generations. Both provide the means to move from the two-dimensional drawings of molecules to accurate three-dimensional portrayals. However, *SpartanModel* offers a number of significant advantages over plastic models.

The first advantage is that *SpartanModel* overcomes the fact that a plastic model kit contains only a limited number of “parts”, perhaps ten or twenty “carbon atoms” and a much smaller number of nitrogen and oxygen atoms. Therefore, only relatively small molecules can be constructed. More importantly, a shortage of parts means that a molecule needs to be disassembled before another molecule can be assembled. This makes it impossible, or in the best circumstances, unnecessarily difficult, to compare the structures of different molecules. *SpartanModel* is unbounded, and molecules with dozens or even hundreds of atoms can be accommodated. Comparisons between different molecules can easily be made.

A related shortcoming of plastic model kits is that they are able to show off just a single aspect of molecular structure, most commonly, the connections (bonds) between atoms. Plastic models that depict overall size and shape are available, but need to be purchased and used separately. On the other hand, models made with *SpartanModel* may be portrayed either to emphasize bonding or to convey information about a molecule’s overall size and shape. A further disadvantage is that plastic models “show” but do not “tell” us about important aspects of molecular structure, for example, about the volume that a molecule requires or its surface area. *SpartanModel* provides both a visual image as well as numerical values for these quantities. Of even greater practical value, *SpartanModel* assigns and displays R/S chirality, both for simple molecules where the rules are relatively easy to apply as well as for complex molecules where even an “expert” would be challenged.

Neither *SpartanModel* nor a plastic model kit is able to build proteins. However, *SpartanModel* connects seamlessly to the on-line Protein Data Bank1 (PDB), providing access to ~60,000 experimental protein crystal structures. A PDB entry is automatically retrieved given its identifier, and displayed as a “ribbon model” (eliminating atomic details so as to emphasize the backbone structure). The model may be manipulated enabling detailed visual inspection.

The second advantage is that the structures obtained by *SpartanModel* are not based on the fixed dimensions of the “parts” as they are with plastic models, but rather result from application of

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quantum mechanics. This means that SpartanModel is actually a predictive tool, not merely one following empirical rules. It can be used to explore chemistry.

The third advantage is that the information provide by SpartanModel is not restricted to molecular structure as it is with plastic models. Energies, atomic charges and dipole moments, molecular orbitals and orbital energies and electrostatic potential maps may be obtained for any molecule. In addition, heats of formation and infrared spectra for approximately 6000 molecules obtained from high-quality quantum chemical calculations (beyond those provided in SpartanModel) are available from a database included with and accessed from SpartanModel. The availability of energies (as well as selected heats of formation) allows the most stable isomer to be identified and to say whether a reaction is exothermic or endothermic. Calculated energies may also be employed to assign the lowest-energy conformation of a molecule and to examine the likelihood that other conformers will be present. The infrared database provides realistic spectra and allows association of individual features in the spectrum with the motions of specific groups of atoms.

In short, plastic models are severely restricted, in terms of the complexity of what can be built, the accuracy of the presentations and in what information they are able to provide.

Some may argue that plastic models are “tried and tested”, and that an electronic model kit is unfamiliar or intimidating. We suspect that the vast majority of students will have the opposite perspective. After all, today’s students have grown up with computers and expect to use them during their college education. In the final analysis, the choice is not between plastic and computer-based models, but whether or not models have something to offer in a chemist’s education. We think that they do.

**GETTING STARTED WITH SpartanModel**

The easiest way to learn how to get started with SpartanModel is to spend an hour to complete the set of tutorials that have been provided. They cover both the use of the program and the interpretation of the quantities that result. Start with Basic Operations, which shows how to manipulate molecules, query molecular properties, display molecular orbitals and electrostatic potential maps and draw infrared spectra. Building molecules and performing quantum chemical calculations is not illustrated, but deferred to Acrylonitrile. This tutorial should be completed next. The remainder of the tutorials can be completed in any order. Camphor and Androsterone illustrate construction of successively more complex organic molecules. The first of these provides another example of displaying an infrared spectrum, and both tutorials illustrate the identification and assignment of chiral (R/S) centers. Acetic Acid Dimer shows how a molecular complex may be assembled and its binding energy calculated. 1,3-Butadiene and trans-Cyclooctene show how energy comparisons among molecules are made. The first involves different conformers of the same molecule and shows how the conformation of a
molecule can be changed. The second involves different stereoisomers. **2-Methylpropene** and **Comparing Acid Strengths** illustrate comparisons of molecular orbitals and electrostatic potential maps for different molecules. Finally, **Hemoglobin** shows how to access the Protein Databank (PDB). A part of this tutorial requires that the user be connected to the internet.

**PROBLEMS KEYED TO ORGANIC SYNTHESIS**

A set of ~60 problems, accessible under Problems in the Welcome screen, has been keyed to the 3rd edition of Organic Synthesis. Many of the problems are made up of text (html) files only, opening up a “blank screen” in SpartanModel. However, some of the problems include materials that cannot be generated with SpartanModel and have been prepared using Spartan. These include problems involving transition states and those using LUMO maps and local ionization potential maps. These materials are “read only” and while the models may be examined and manipulated and measurements taken, they may not be altered.

The instructor is free to make additional tutorials and problems using Spartan, and to add these to the existing collections. Instructions are provided under Adding Tutorials and Problems under the Help menu.

**TECHNICAL OVERVIEW OF SpartanModel**

SpartanModel may be viewed in terms of its components: a molecule builder including a molecular mechanics based scheme for preliminary structure refinement, a real-time quantum chemical engine and two databases.

SpartanModel’s builder uses atomic fragments (for example, sp, sp² and sp³ carbon fragments), functional groups (for example, amide and carbonyl groups) and rings (for example, cyclohexane and benzene). Some molecules can be made in just one or two steps (“mouse clicks”), while most others require fewer than ten steps. For example, few than 20 steps are required to build the steroid androsterone, the most complicated molecule provided in a tutorial that accompanies SpartanModel. Once constructed, molecules can be displayed as to depict bonding (as with most types of plastic models) or overall size and shape (so-called space-filling or CPK models). Associated with the builder is a simple “molecular mechanics” procedure to provide a refined geometry as well as measurement tools for bond distances and angles, volumes, surface areas and polar surface areas (of space-filling models) and for assignment of R/S chirality.

The quantum chemical engine provided in SpartanModel may be used to obtain the geometries and properties of the vast majority of molecules encountered in elementary organic chemistry. The desire for open-endedness (any “reasonable size” molecule may be calculated) together with practical concerns, requires use of a very simple quantum chemical model. The procedure
used in \textit{SpartanModel} involves two quantum chemical steps and is preceded by a molecular mechanics\textsuperscript{2} step to ensure a reasonable starting geometry. The first quantum chemical step is calculation of geometry using the PM3\textsuperscript{3} semi-empirical model and the second step is calculation of the energy and wavefunction at this geometry using the Hartree-Fock 3-21G\textsuperscript{4} model. The resulting wavefunction is used for calculation of the dipole moment and atomic charges and (if requested) graphical displays of the molecular orbitals and electrostatic potential map. PM3 geometry calculations and 3-21G energy calculations for molecules comprising up to 30-40 heavy (non-hydrogen) atoms are likely to require less than one minute on a present day Windows or Macintosh computer.

The quantum chemical calculations in \textit{SpartanModel} properly account for geometry and provide a sound basis for graphical displays of molecular orbitals and electrostatic potential maps. They also provide a qualitatively accurate account of the energies of most types of chemical reactions as well as conformational energy differences. Heats of formation for \(~6000\) molecules obtained from the T1\textsuperscript{5} thermochemical recipe and included in a database can be used to supplement calculated energies where higher accuracy may be necessary. T1 has been shown to reproduce experimental heats of formation with an rms error of \(~8\) kJ/mol.

The second database contains infrared spectra for \(~6000\) molecules obtained from the EDF2\textsuperscript{6}/6-31G* density functional model, adjusted to account for known systematic errors and for finite temperature. The resulting spectra are visually and quantitatively very similar to observed infrared spectra. Vibrational modes associated with individual lines in the spectrum may be “animated”.

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