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Computers in Chemistry

Using Java to Animate the Vibrations of Molecules: Calculation and Visualization of Molecular Vibrations in $(NSF)_3$

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Animation of molecular vibrations can greatly aid in the physical understanding of vibrational spectroscopy…

The ability to animate molecular motion and interactively rotate the system in three-dimensional space is extremely helpful in communicating chemical concepts such as reactions and molecular vibrations. Here, we present a Java program and a chemical plug-in that allows the animation of molecules within popular world wide web browsers. To illustrate the usefulness of animation as a visualization aid, the molecular vibrations of $(NSF)_3$ are simulated using a general atomic and molecular electronic structure system (GAMESS).

Introduction

The ability to animate chemical motion is a standard feature in numerous software programs [1]. Through definition of a mime type and helper applications, software programs can

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be invoked to display a chemical structure. The software must first reside on the user's computer, however, and the program is executed separate from the browser. To view molecules or animations within a browser, third party plug-ins can be installed to work with specific web browsers. Chemscape Chime [2] is an example of a plug-in for the Netscape browser that allows molecules to be viewed, rotated and animated. The use of software programs and plug-ins is limited to specific operating systems and architectures in which these programs were designed, and they must be installed separately from the browser. Sun Microsystems Java programs are executed within the framework of the web browser, therefore, any Java enabled browser (e.g. Netscape and Microsoft Explorer) can run the byte code. A molecular viewer has been written in Java by Sun Microsystems that allows molecules to be viewed within a web browser [3]. We have modified this program to read in and cycle through multiple xyz files. The Java applet is designed to animate molecules while allowing the viewers perspective to change through interactive rotation of the system. To illustrate the use of the animated Java applet as well as other chemical viewers, we present simulated vibrations of $(NSF)_3$ as an example of how three-dimensional rendering can aid in conceptual understanding of molecular motion.

Java Programming Language

Sun Microsystems Java programming language is similar in structure to C++. Compiled Java programs, called applets, are executed within the framework of a compatible browser and are, therefore, independent of machine architecture, allowing an applet to run on any browser supported system. This is a necessity for the internet, where all computers must be able to access the same information. Java is supported by Netscape and Microsoft Explorer and does not require any additional software to be installed therefore, anyone browsing the web is able to view Java applets without further modification to their installed browser. Also, Java compilers and manuals are free programs, allowing any person to download the software and develop their own Java programs. The Java developer's kit (JDK 1.1) can be downloaded as a single self-extracting executable file and provides all the instructions, libraries, and compilers needed to develop Java applets [3]. Included with the JDK is a number of sample applets. The molecular viewer applet, which was used as a template for our animated viewer, is one of these original samples. At present, Java programs often suffer from slow execution. This is the consequence of not being optimized for a given computer

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architecture and is currently being addressed by the development of accelerators for individual computer systems.

Java Molecular Animator

The original Molecular Viewer Java applet written by James Gosling read in one xyz data set and displayed it in ball format. The Molecular Viewer also allowed the user to rotate the molecule to see different perspectives. There are many viewers, both commercial and public, that allow the display and animation of molecules. We used the existing code from the Molecular Viewer and modified it to allow for animation of molecules. Instead of reading in one *xyz* data set, the Java Molecular Animator reads in multiple *xyz* data sets. Each data set has a standard *xyz* format, and they each reside in their own file. The Java Molecular Animator consists of three Java classes. Two of them, XYZChemModel and Atom, remain unchanged from the Moleculer Viewer. These classes are used to define a XYZ model object. The third class, XYZApp, uses the other classes to read in an xyz data set, create an XYZ model object, and paint it on a web page. In order to animate the molecules, we modified the XYZApp class to read in multiple data sets, then paint them in succession. The end result is animation. The modifications to XYZApp can easily be extended to read in any number of data sets. We made several different versions of the class to read in 2 data sets, 5 data sets, and 10 data sets. The XYZApp class that reads in each data set can be used to display any number of xyz-file frame animations. The complete Java source code, HTML linking files, executable files, and xyz data sets are available on this article's abstract page. All files are contained in the single compressed file java_jy.zip.

Animating Vibrational Modes

Students often complain that textbooks frequently give examples of very simple systems and leave the more complicated examples without explanation. Teaching the fundamentals of molecular vibrations is usually accomplished by using examples of molecular vibrations in water, carbon dioxide, hydrochloric acid, or some other simple molecule that can be represented easily in a textbook. These molecules are used to teach vibrational concepts because visualization of more complex examples is impaired by instructing from the blackboard or out of a textbook. Computer animation allows more complicated molecular vibrations to be viewed and used for student instruction. To give students a more involved example of molecular vibrational modes in solids, we use the

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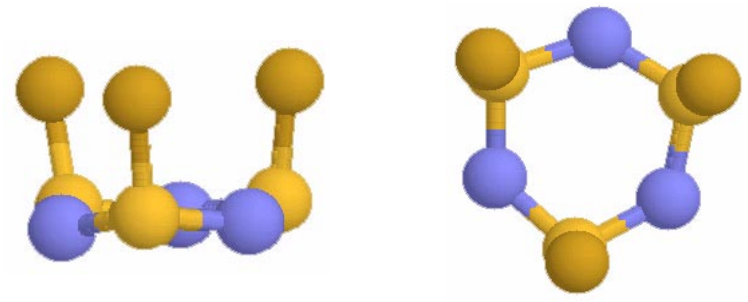

FIGURE 1. BALL-&-STICK REPRESENTATION OF MOLECULAR $(NSF)_3$ FROM TWO DIFFERENT PERSPECTIVES.

molecular trimerized thiasyl fluoride $(NSF)_3$ as a model. As shown in Figure 1, $(NSF)_3$ has "crown-like" conformational trimers consisting of an alternating nitrogen and sulfur puckered six-fold ring with fluorine atoms bonded to the sulfur (C_{3v} point group symmetry). The nitrogen is shown in blue, the fluorine in orange and the sulfur in yellow. X-ray diffraction experiments on both the free-molecular and solid phases reveal a peculiar bonding arrangement for the trimer [4]. Theoretical calculations indicate that the sulfur atoms are overbonded, while the nitrogens are underbonded in this configuration. The molecular units form a hexagonal crystal having a space group *R3c* with a = 10.238 and c = 9.535 [5]. The large separation between individual molecules (2.93Å for F…F closest approach) indicates that the intermolecular bonding in the crystal is not covalent in character, but is determined by van der Waals' forces; therefore, we can consider $(NSF)_3$ a molecular solid and only consider the vibrations of the individual molecular units.

The quantum chemistry package GAMESS (General Atomic and Molecular Electronic Structure System) can be used to calculate the harmonic vibrational properties of molecules [6]. The most recent implementation of this code includes a number of semi-empirical basis sets including PM3, which is well suited to the treatment of sulfur, nitrogen, and fluorine containing compounds [7]. In particular, the geometries generated by this method are of similar accuracy to those determined by much more sophisticated calculations. One of the most useful features of this code is that MNDO, AM1, and PM3 semi-empirical wavefunctions are available internally for use in exploratory structural studies. Although these models are often used to generate starting geometries for subsequent higher-level quantum-mechanical calculations, they possess an impressive predictive power of their own. They have recently been used with great success in quantitatively modeling a wide range of physical and chemical systems including the

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TABLE 1. Simulated molecular vibrations in $(NSF)_3$ using GAMESS with a PM3 semi-empirical Hamiltonian (clicking on any of the individual bands colored in red will run the Java applet vibrational animation).

Band	Frequency (cm^{-1})
1, 2	97
3	136
4	273
5, 6	327
7, 8	457
9, 10	550
11	591
12	734
13, 14	768
15, 16	803
17	806
18	854
19	1020
20, 21	1306

vibrational properties of sulfur compounds [7], the interaction of water with zinc oxide surfaces [8], hydrogen-bonded systems [9], and dehydroxylated silica networks [10].

In the present work, we explore the harmonic vibrational properties of the $(NSF)_3$ molecule using the quantum chemistry package GAMESS. Employing a semi-empirical molecular orbital method (PM3) with no geometric constraints the 21 ($3N$-6) molecular vibrations of $(NSF)_3$ are calculated and listed in Table 1. A detailed description of the procedure used to calculate the harmonic vibrational modes is given in Appendix A. A compiled list of all the vibrations in molecular $(NSF)_3$ is given above.

From these models the symmetry (e.g., A_1, E) and type of vibration (e.g., bending, stretching) can be assigned to each individual mode. In particular, we find that the spectral features in the range between 100 and 600 cm^{-1} correspond to out-of-plane (S–N plane) breathing modes. Modes in the frequency band from 700 and 900 cm^{-1} are the

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TABLE 2. The correlation between the site and molecular species for all the atoms in $(NSF)_3$ ($Z = 9$).

Site Symmetry				Molecular Symmetry	a_γ	
f^γ	t^γ	C_s	$\xrightarrow{\sigma_V}$ correlation	C_{3v}	$a_\zeta = a_{A'} + a_{A''}$	
18	2	A'	→	A_1	$2M_V$	$2M_V+0$
9	1	A''	→	A_2	M_V	$0+M_V$
			→	E	$3M_V$	$2M_V+M_V$

most intense and correspond to symmetric stretching, while the weak higher-frequency features above 1000 cm^{-1} appear to be related to S–N stretching. Of the 21 vibration modes, there are only 14 nondegenerate vibrations. This is due to the C_s site symmetry of the individual atoms. The correlation table for molecular $(NSF)_3$ with site symmetry, C_s, and molecular symmetry, C_{3v}, is shown in Table 2. In Table 2, t^γ is the number of translations, a_ζ represents the sum of the degrees of freedom contributed by each site species γ to a factor group species ζ, and f^γ is the degrees of vibrational freedom present in each site species γ, for an equivalent set of atoms. f^γ is related to t^γ by the following equation;

$$f^\gamma = t^\gamma \times n \tag{1}$$

where n is the number of atoms in an equivalent set [11]. Once the correlation table is known, the irreducible representation for all normal vibrations ($\Gamma^{mol\ vib}$) can be extracted [12]. The normal vibrations of $(NSF)_3$ are shown in Table 3. There are 14 modes in the irreducible representation, which agrees with the total number of non degenerate vibrational modes calculated using no geometric constraints in a GAMESS simulation. These results can be compared with the experimental spectrum to help elucidate the vibrational modes and the nature of the bonding within a molecule or crystalline unit cell.

The vibrational animation described in this paper involves two distinct steps: (1) The generation of *xyz*-style data for the animator input and (2) the action of the Java animator or chemical viewer on that data, leading to the final animation sequence. In the present

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TABLE 3. The irreducible representation of the normal vibrations of $(NSF)_3$.

a_ζ, species coefficient

	A_1	A_2	E
Γ^N	2	1	3
Γ^S	2	2	3
Γ^F	2	1	3
$-\Gamma^{rot}$	–	-1	-1
$-\Gamma^{trans}$	-1	–	-1
Γ^{mol}_{vib}	5	2	7

$$\Gamma^{mol\ vib} = 5A_1^{(R,\,IR)} + 2A_2 + 7E^{(R,\,IR)}$$

example, the GAMESS program was used to generate the vibrational eigenvectors of the harmonic dynamical matrix for the molecule. These were trivially manipulated to generate the requisite *xyz* data for input to the Java animation script using a short program (eig.f). Other programs can easily be adapted to generate *xyz* data in a frame-by-frame sequence. This aspect of our procedure is certainly not new; many commercial and public domain quantum chemistry programs have their own internal schemes for generating vibrational eigenvectors and atomic coordinates.

The separation of the animation process into the elements described above was imposed so that other program packages could be used to generate the input animation data. Crude input data can even be generated by hand. An instructive exercise for students would be to animate a diatomic molecular vibration by simply perturbing the equilibrium atomic coordinates with out-of-phase sinusoidal displacements. Since the Java animator and the Chime plug-in can act directly on such an input file, it provides a convenient exploratory interface for students.

The ability to easily simulate and visualize vibrational modes on a computer or over the internet provides a unique opportunity for students to obtain a physical and conceptual understanding of vibrational spectroscopy. This type of exercise is meant to act as a prelab to either IR or Raman spectroscopy undergraduate laboratory experiments. The

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vibrational animation files (*xyz* files) can be downloaded for aid in a more visual representation. However, if a more rigorous theoretical basis is desired, students can optimize the geometry and do the simulations on their own molecule by downloading the free GAMESS software and generating their own *xyz* files.

Conclusion

Through freely available simulation packages and an animated viewer, the concepts of molecular and lattice vibrations can be shown to a student in a visual representation that is not available in laboratory projects. Having simulations and visual models available on the internet allows students and instructors to access the information in a convenient format that does not require a costly workstation environment.

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