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Journal of Chemical and Pharmaceutical Research

J. Chem. Pharm. Res., 2010, 2(1): 147-154

ISSN No: 0975-7384

Knowing How Each Atom Moves in Real-Time During Chemical Reactions

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Abstract

The Raman Effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. It therefore provides a fingerprint by which the molecule can be identified.A new spectroscopy technique to uncover the precise sequence of atomic movements and structural changes that occur during complex chemical transformations. GFP involves a classic intermolecular proton transfer reaction to produce its fluorescent form. This happens on an ultra fast timescale - from 10 femtoseconds to 10 picoseconds. To perform structural measurements and determine the mechanism and pathway of any reaction occurring in this time range by using femtosecond stimulated Raman spectroscopy (FSRS). A great deal was known about the kinetics of the proton transfer reaction but little was known about the actual complexity of the reaction coordinate or combination of atomic motions that must occur before the proton can be transferred. The time resolved structural data which told us the actual atomic motions that are necessary. 'This work shows a possibility that we will be able to know how structure changes in real-time even in very complex molecules like a protein using FSRS.

Raman Spectroscopy

The Raman Effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman Effect, a photon excites the molecule from the ground state to a virtual energy state. When the molecule emits a photon and returns to the ground state, it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation wavelength[1].

If the final state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an Anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction[2].

A change in the molecular polarization potential or amount of deformation of the electron cloud with respect to the vibrational coordinate is required for a molecule to exhibit a Raman Effect. The amount of the polarizability change will determine the Raman scattering intensity. The pattern of shifted frequencies is determined by the rotational and vibrational states of the sample. Raman spectroscopy is commonly used in chemistry, since vibrational information is specific to the chemical bonds and symmetry of molecules. It therefore provides a fingerprint by which the molecule can be identified[3].

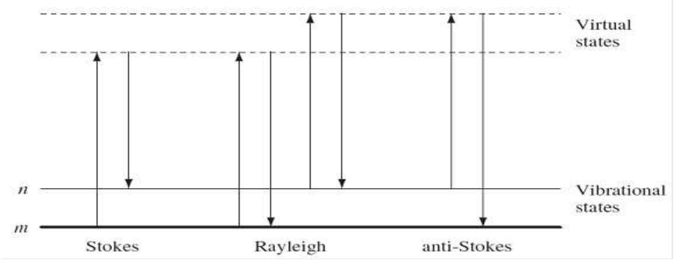


Fig.1.Energy levels in Raman Spectroscopy

Femtosecond broadband stimulated Raman spectroscopy (FSRS) is a new technique that produces high-resolution (time-resolved) vibrational spectra from either the ground or excited electronic states of molecules, free from background fluorescence[4].

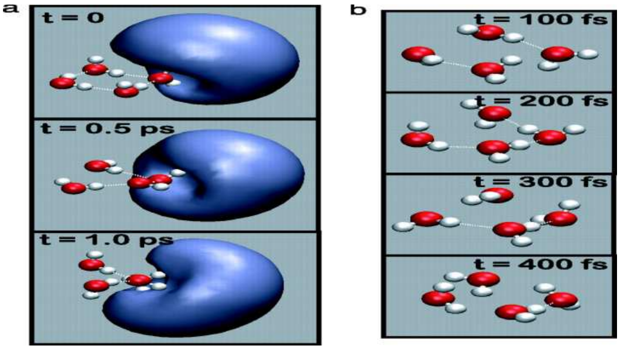


Fig.2.Example of Femtosecond broadband Raman spectroscopy

FSRS uses simultaneously a narrow bandwidth ~1–3 ps Raman pump pulse with a continuum ~30–50 fs Stokes probe pulse to produce sharp Raman gains, at positions corresponding to vibrational transitions in the sample, riding on top of the continuum Stokes probe spectrum. When FSRS is preceded by a femtosecond actinic pump pulse that initiates the photochemistry of interest, time-resolved Raman spectroscopy can be carried out. We present two theoretical approaches to FSRS: one is based on a coupling of Raman pump and probe light waves with the vibrations in the medium, and another are a quantum-mechanical description[5].

The latter approach is used to discuss the conditions of applicability and limitations of the coupled-wave description. Extension of the quantum-mechanical description to the case where the Raman pump beam is on resonance with an excited electronic state, as well as when FSRS is used to probe a nonstationary vibrational wave packet prepared by an actinic pump pulse[6,7].

Nature of Molecules

A molecule is defined as an electrically neutral group of at least two atoms in a definite arrangement held together by very strong (covalent) chemical bonds[8,9]. Molecules are distinguished from polyatomic ions in this strict sense. In organic chemistry and biochemistry, the term molecule is used less strictly and also is applied to charged organic molecules and biomolecules.

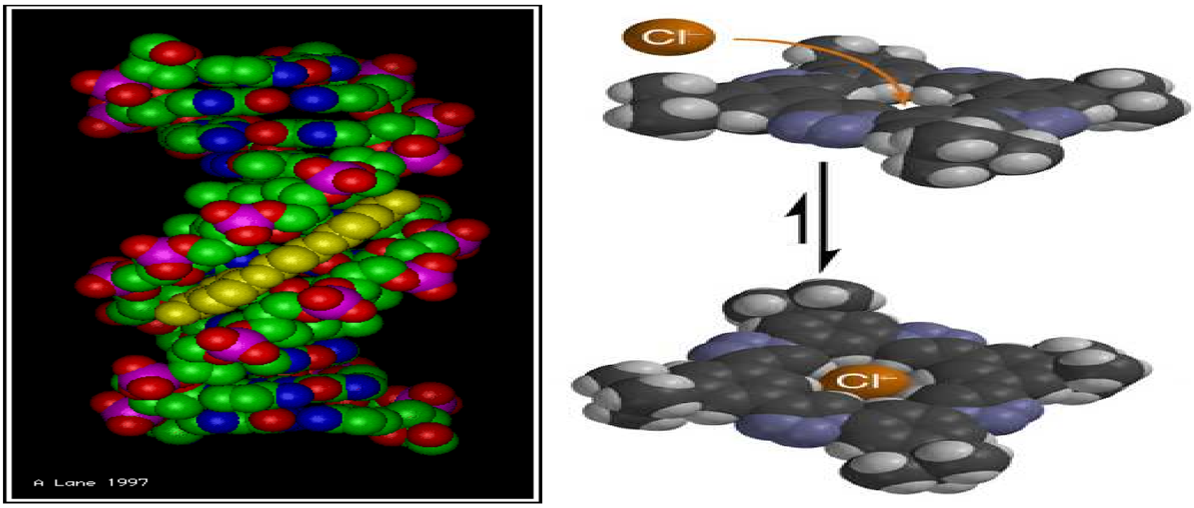


Fig.3. Complex molecule

When elements combine to form a compound, the properties of the compound are determined from the properties of the MOLECULE of the substance. The molecule, then, is the building block of a compound, just like the atom is a building block of the element. The molecule is the smallest portion of a compound that can be isolated and still retain the properties of the compound[10]. A molecule is depicted in various ways; here are a few:

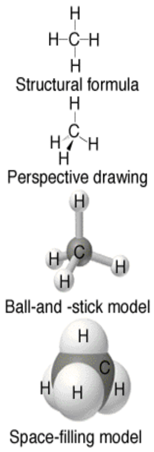


Fig.4.Different ways to depict a molecule

Molecules are made up of two or more atoms, either of the same element or of two or more different elements, joined by one or more covalent chemical bonds. According to the kinetic-molecular theory, the molecules of a substance are in constant motion[11-13]. The state (solid, liquid or gaseous) in which matter appears depends on the speed and separation of the molecules in the matter. Substances differ according to the structure and composition of their molecules. A molecular compound is represented by its molecular formula; for example, water is represented by the formula H2O. A more complex structural formula is sometimes used to show the arrangement of atoms in the molecule[14].

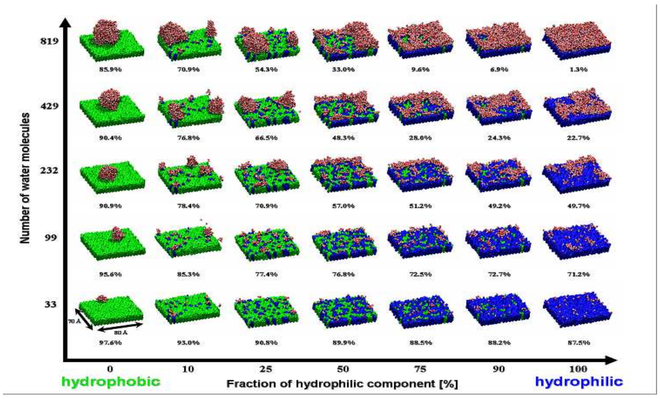
Molecules differ in size and molecular weights well as in structure. In a chemical reaction between molecular substances, the molecules are often broken apart into atoms or radicals that recombine to form other molecules, i.e., other substances. In other cases two or more molecules will combine to form a single larger molecule, or a large molecule will be broken up into several smaller molecules[15].

Molecular simulations of aqueous and soft surfaces and interfaces (air/water, air/ice, air/organic, water/organic etc.) and solute-solvent interactions in interfacial environments, in particular those of atmospheric relevance[16]. The aim is to understand at a molecular level the fundamental interactions governing the physics and chemistry of the interfacial processes and to provide physically justified input for the atmospheric models to advance our understanding of air quality issues and global climate change.

Some examples are given below:

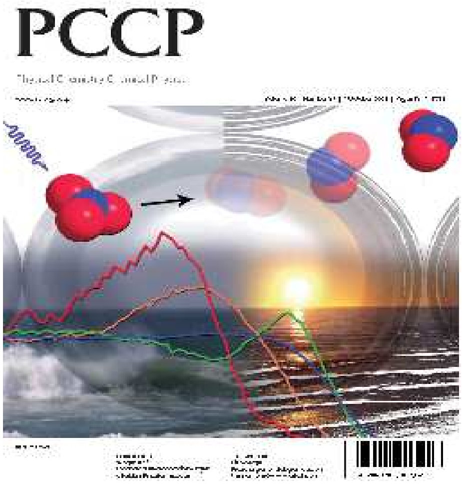
1. Microscopic wetting of heterogeneous organic surfaces

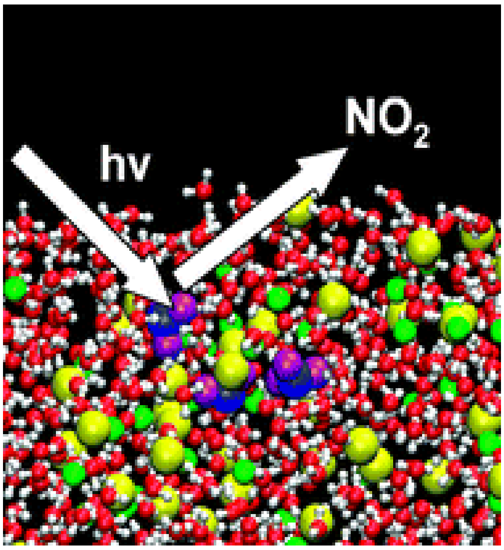
Matrix of snapshots from molecular dynamics simulations of water on self-assembled monolayer of alkanethiols on gold as a function of the fraction of COOH terminated alkanethiols (along the x-axis) and number of water molecules wetting the SAMs (along the y-axis). The fraction of non-wetted surface area of each system is indicated below the corresponding snapshot. Color coding: methyl terminated alkanethiols-green, COOH-terminated alkanethiols-blue, water oxygen-red, water hydrogen-white[17].



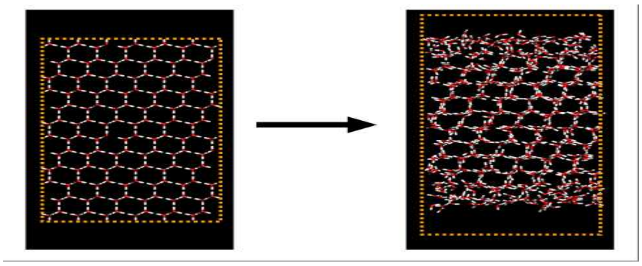
2. Photochemistry of nitrate in sea salt aerosol particles

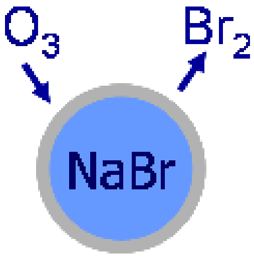
This study shows the complex interactions between chloride, sodium and nitrate ions resulting in enhanced photolysis of nitrate in the mixed salt solution droplets compared to pure NaNO3 solution droplets. Color coding: Chloride-yellow, sodium-green, nitrate-blue (nitrogen) and purple (oxygen), water-red (oxygen) and white (hydrogen)[18].



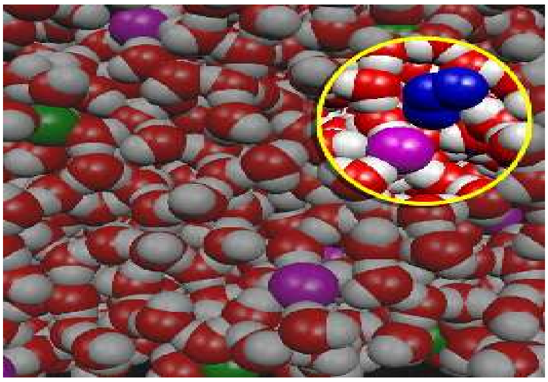


3. Ice-vapor interaction via the quasi-liquid layer on the surface of ice. Snapshots from molecular dynamics simulations of ice: perfect ice crystal (initial condition of the simulation) on the left, ice slab with two open surfaces at 250 K on the right[19].





4. Oxidation of NaBr aerosol particles by ozone



This snapshot from a molecular dynamics simulation aimed at elucidating the mechanism of bromine production from the reaction of ozone with aqueous NaBr aerosol particles shows an ozone molecule (blue) in contact with a bromide ion (purple) at the surface of 1.2M NaBr solution. Sodium ions are depicted in green, oxygen atoms in red, hydrogen atoms in grey[20].

Structural snapshots of complex molecules

A new spectroscopy technique to uncover the precise sequence of atomic movements and structural changes that occur during complex chemical transformations. The scientists used the new method to pin down the changes that occur when green fluorescent protein (GFP) glows under blue light, and say the approach could be used to further understand important chemical transformations in other complex molecules, as well as tailor new molecules. GFP involves a classic intermolecular proton transfer reaction to produce its fluorescent form[21]. This happens on an ultra fast timescale-from 10 femtoseconds to 10 picoseconds. Previously, it had been extremely difficult to perform structural measurements and determine the mechanism and pathway of any reaction occurring in this time range. But using femtosecond stimulated Raman spectroscopy (FSRS). A great deal was known about the kinetics of the proton transfer reaction but little was known about the actual complexity of the reaction coordinate or combination of atomic motions that must occur before the proton can be transferred. The time resolved structural data which told us the actual atomic motions that are necessary[22,23].

The structural changes by obtaining vibrational spectra of the GFP chromophores-the part of the molecule responsible for its color-after it was raised to an excited electronic state by photon absorption. As the molecule proceeds along its chemical reaction coordinate, which is a result of protons transferring from one residue to another, the team could monitor the molecular vibrations[24,25].

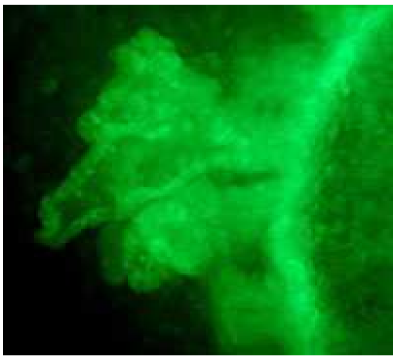


Fig.5.Green fluorescent protein

The reaction coordinate was found to comprise the complex motion of many atomic groups in addition to the proton that is transferred. 'This complexity has long been predicted, but it was very difficult [or] impossible to directly observe experimentally until our development of the time resolved stimulated Raman technique, Since this new approach allows scientists to observe the atomic motions that occur after a molecule absorbs a photon it could potentially be important in the development of photovoltaic devices and dye sensitized nanoparticles that are used to convert light into electricity[25-30]. Knowing how each atom moves in real-time during chemical reactions has been a dream of chemists. 'This work shows a possibility that we will be able to know how structure changes in real-time even in very complex molecules like a protein - using FSRS.

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