NANOSPECTROSCOPY OF MATERIALS AND BIOMEDICINE AT FUNDAMENTAL ATOMIC AND MOLECULAR SCALES

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ABSTRACT

Spectroscopy is the most powerful and precise tool to study matter. Physical and chemical properties at fundamental atomic and molecular scales are the natural basis of nanoscience and nanotechnology as atomic-molecular sizes are 0.1 – 1 nanometer. Each element or compound has a unique spectral signature. Electromagnetic radiation in various wavelength bands from X-ray to Infra-red can be used to probe material and biological structures through spectral transitions in atoms and molecules. Such studies will provide the foundation for basic understanding as well as practical applications for (A) construction of new composite materials, and (B) radiation diagnostics and therapy using nanomedicine. Inner shell transitions that arise from a core electron being promoted into an outer orbital via the absorption of a photon with energy resonant to that transition account for the greatest absorption of energy. Calculations to determine the energies for such transitions in atomic oxygen as well as water are presented.

Nanospectroscopy

- Nanoscale: Nanometer (nm); Atomic/Molecular Size ~ 0.1 – 1 nm
- Broadband imaging yields pictures but not detailed microscopic information
- Spectroscopy is far more powerful and precise: "A spectrum is worth a thousand pictures"
- Every atom or molecule has a spectral signature → Every object has a unique spectral code
- Large-scale quantum mechanical calculations and/or experiments to decipher the code
- Tune radiation source to resonant energies for optimum absorption
- Optimize fluorescent emission following inner-shell excitation and resonant breakup

Nanospectroscopy Applied to Nanobiomedicine: Resonance Targeted Therapy of Cancerous Tumors

The Need for Nanobiospectroscopy:

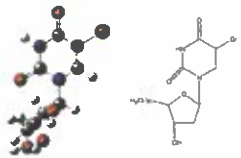
- Full body CAT scans use high energy broad band X-rays with very high radiation dosages, comparable to Hiroshima I (N.Y Times, Sep. 6, 2004)
- Spectroscopically targeted radiation should be far more efficient with reduced exposure
- Radiosensitized breakup of DNA of tumor cells, minimize dosage to surrounding normal tissue
- Heavy high-Z elements absorb/emit X-rays at higher energies where light "biogenic" elements (H,C,N,O → CHON) elements are increasingly transparent
- Maximize energy deposition by targeting spectral windows in high Z atoms injected
- Tumors could be radiosensitized by halogenated thymidine analogs such as BUdR

Two potential pathways to be demonstrated

1. Direct X-ray impact and absorption at resonant spectral windows
2. Fluorescent emission due to inner-shell ionization following brief impact from high energy X-ray destroy tumor cells locally

Figure 1: Treating Cancer using Nanoparticles

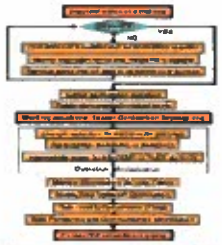
Figure 2: Structure of Bromodeoxyuridine BUdR



Code Development Tools: The Tensor Contraction Engine

- The Tensor Contraction Engine will allow the next generation of atomic and molecular physics codes to be developed efficiently, taking advantage of large scale parallel processing.
- It is based upon object oriented symbol manipulation, such that the user need not be familiar with lower level parallel programming.
- The user enters expressions for the high level tensor contractions involved, in a near mathmatical format. TCE produces the parallel code.
- Quick development of the next generation of codes will allow the lower part of the periodic table, and complex molecular problems to be explored more rapidly.

Figure 4: Flowchart of the Tensor Contraction Engine (TCE)

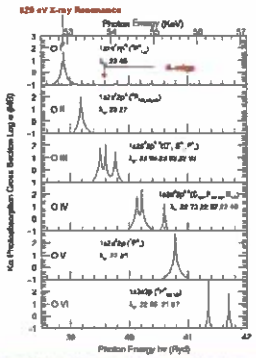


Nanospectroscopy: Inner shell resonant absorption in atomic Oxygen

X-ray absorption by Oxygen ions occurs most efficiently at discrete resonant energies, as demonstrated in large-scale calculations carried out at the Ohio Supercomputer Center using the R-matrix method.

- Resonances in Oxygen Ions, from neutral O I to Li-like O VI
- Photoabsorption cross section at resonant energies is more than two orders of magnitude higher than at background energies, including the K-edge
- The 529 eV resonance in neutral O I has about 100 times the background cross section, hence more energy will be absorbed at this wavelength!

Figure 5: Photoionization cross sections of various Oxygen atoms



Nanospectroscopy: Inner shell resonant absorption in water

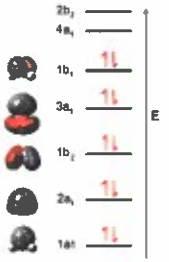
Structural Parameters

$r_{OH} = 0.959Å$

$\theta_{HOH} = 104.5°$

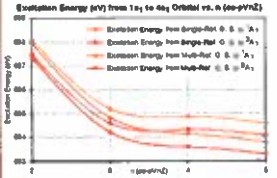
X-ray absorption by Oxygen the in water should also occur most efficiently at resonances, like the atomic case. These resonance positions will change position and change however due to the fact that the molecular 1 electron orbitals are best expresed as a linear combination of the atomic oxygen 1 electron orbitals and 1 electron orbitals from the hydrogen atoms. While the lowest lying orbital closely corresponds to the oxygen 1s orbital, the valence orbitals involved in bonding are quite different that the Oxygen 2s and 2p orbitals. Calculations on this system were carried out using the COLUMBUS package of quantum Chemistry codes.

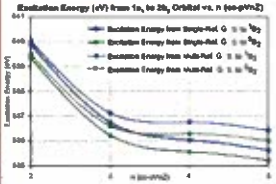
Figure 6: Contors (and symmetry designations) of the occupied orbitals in the ground state of water



Nanospectroscopy: Inner shell resonant absorption in water (continued from previous column)

Figure 7 & 8: Contors (and symmetry designations) of the three orbitals involved in the four (two singlet, two triplet) X-ray absorption transitions out of the ground state of water, along with the transition energy as a function of basis set used.





Nanospectroscopy: Comparison of inner shell resonance positions between atomic Oxygen and water.

Atomic Config. and Term Symbol	Energy above ground state	Energy averaged over J values	Molecular Config. and Term Symbol	Energy above ground state (multireference cc-pV5Z)
$1s^1 2s^2 2p^5\ ^1P_1$	528.8 eV	528.8 eV	$1a_1^1 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^{1\,1}A_1$	534.6 eV
			$1a_1^1 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^{1\,3}B_2$	536.4 eV
$1s^1 2s^2 2p^5\ ^3P_1$	528.8 eV	528.8 eV	$1a_1^1 2a_1^2 1b_2^2 3a_1^2 1b_1^2 4a_1^{1\,3}A_1$	534.1 eV
$1s^1 2s^2 2p^5\ ^3P_2$	528.8 eV		$1a_1^1 2a_1^2 1b_2^2 3a_1^2 1b_1^2 2b_2^{1\,3}B_2$	536.0 eV