Molecular Dynamics by X-rays?

T. Prevenslik

QED Radiations, Discovery Bay, Hong Kong
thomas@nanoqed.org

1. Introduction – Recently, RIXS is shown [1] to excite specific types of vibrational motion. Externally supplied X-rays are tuned to the symmetric stretching of a molecule while other tunings excite bending modes. RIXS stands for resonant inelastic X-ray scattering spectroscopy. More fundamentally, RIXS suggests the long-standing paradigm that chemical reactions are initiated by changes in positions of atoms in molecules depending on their temperature needs to be revised to one based on positional changes by X-rays. Specifically, the equipartition theorem in MD that defines atomic vibrations from atom temperatures is no longer valid and needs to be modified from thermal heat changing atom temperatures to thermal heating of atoms producing X-rays. In this paper, the nitrogen molecule is used as a simple example of how MD may be modified for X-ray initiated chemical reactions in complex molecules.

2. Background - MD based on statistical mechanics for a continuum of molecules cannot simulate chemical reactions because atoms in discrete molecules are incorrectly assumed to have heat capacity allowing temperature induced positional changes caused by thermal heat. However, the Planck law of QM precludes atoms in discrete molecules from having the heat capacity to conserve thermal heat by an increase in temperature. QM stands for quantum mechanics**.**

3. X-ray Mechanism - Lacking heat capacity by QM, thermal heat cannot increase core electron temperature with conservation proceeding by increasing the electron energy E. Treating the electron [2] as a continuous ring of radius R, the energy $E = hc/2\pi R$. The K-edge absorption for the nitrogen atom having electron energy E = 0.434 keV corresponds to an electron ring radius R = 469 pm. Heat flow Q into the electron is estimated from that into a spherical cavity of the ring radius R in a water bath at ambient temperature T, $Q = 4\pi\Theta RT$. Here, Θ is the thermal conductivity, Θ = 0.61 W/m-K and T = 310 K. Hence, $Q = 1.11 \times 10^{-6}$ J/s and the time τ to fill the K-edge is, $\tau = E/Q$ = 62 ps. The X-ray emission then excites other atoms including 50 meV phonons and charge transfer > 2 eV as depicted in Figure 1.

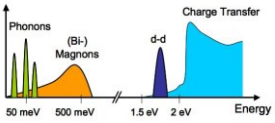

Figure 1. MD by X-rays

4. Application and Results – Standard MD programs are modified for QM by updating atom velocities at each iteration depending on the direction of X-rays emitted and absorbed from all atoms, but temperature fluctuations are excluded consistent with QM. Half of the nitrogen molecule in the stretch mode is simulated by fixing the central anti-node of the molecule. Depending on the inelastic energy Eo absorbed, the X-ray from one atom in the nitrogen pair imparts an initial velocity V to the other atom along the longitudinal direction, $V = \sqrt{(2\ Eo/m)}$, where m is the mass of the nitrogen atom and $Eo = \eta E$, $\eta << 1$. For inelastic X-ray energy Eo = 10 meV, the initial velocity V = 371 m/s. The MD solution was obtained at temperature of 310 K for 20,000 iterations at time step 1×10^{-16} s and found to agree with theory. To provide a comparison with QM, the MD solution by the equipartition theorem was also derived for the nitrogen molecule in the stretch mode. The temperature was adjusted by scaling the velocity to 310 K at each time step. However, the results differed significantly from theory with the temperatures fluctuating +/- 400 K around 310 K contrary to QM.

Also, RIXS response showing phonon excitation (0.2 eV) superposed on the core electron (434 eV) was confirmed with a harmonic response analysis for a 2 DOF model of the nitrogen atom and core electron.

5. References

[1] R. C. Couto, et al., "Selective gating to vibrational modes through resonant X-ray scattering," Nature Comm., 8, 14165, 2017

[2] D. Bergman, Electron Wave Function - Electromagnetic Waves Emitted by Ring Electrons, Foundations of Science, 2005.

Thomas V. Prevenslik is a retired American living in Hong Kong and Berlin. Because classical physics does not work at the nanoscale, he developed a simple theory of QED based on QM. Differing from the complex QED advanced by Feynman and others, simple QED deposits absorbed heat almost entirely in NP surfaces because of their high surface-to-volume ratios. Thus, NP atoms are placed under high EM confinement over nanoscale wavelengths that by the Planck law of QM precludes the atoms from having the heat capacity to conserve heat by an increase in temperature. Simple QED then converts the surface heat into standing EUV radiation inside the NPs with lower quantum states such as plasmon resonances excited by fluorescence. In the instant topic of MD by X-rays, emphasis shifts from atoms in NPs to core electrons in individual atoms. Similarly, QM precludes the core electron to conserve low-level thermal heat from the surroundings by an increase in temperature, and instead the energy level of the core electron increases. But once the core electron energy level reaches the K-edge, the corresponding X-ray is emitted to excite vibrational modes of atoms thereby providing the changes in atomic positions necessary to initiate chemical reactions between reactant molecules. X-ray emission following core electron filling forever repeat.