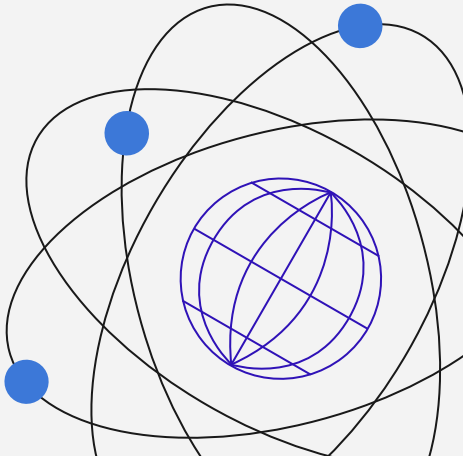
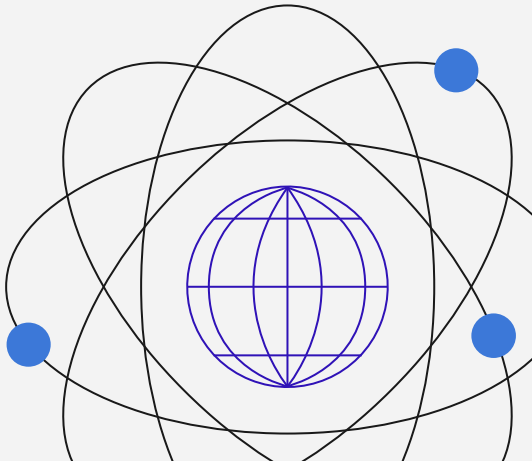
Monte-Carlo Simulation of Radiation-Induced Molecular Decomposition of Water using a Molecular Mechanics Force Field

By: Gary Patterson and Suraj Rao



01 Introduction

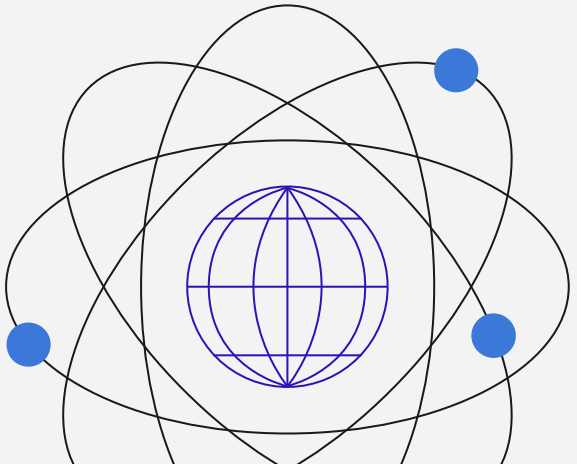
- **What:** Modeled number of neutron + water reactions in a Nuclear Reactor core
- **Why:** Understanding water decomposition is important for reactor energetics, efficiency, and safety.
- **Why:** Allowed us to explore our interests of Nuclear Reactor workings and Force Fields



02

Molecular Mechanics Force Fields

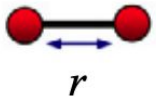
- System of equations and parameters to model molecules.
- Use classical physics to calculate potential energy and forces on atom
- Applied in molecular dynamics simulations and structure prediction
- MMFF94 exhibits accuracy for small organic molecules (like H2O!)



MMFF94 Force Field

$$E_{MMFF94} = \Sigma E_{Bond} + \Sigma E_{Angle} + \Sigma E_{Torsion} + \Sigma E_{OOP} + \Sigma E_{vdW} + \Sigma E_{q}$$

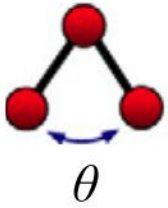
Bond stretch



$$\frac{1}{2}kb_{ij}(r - r_{eq})$$

...

Bond angle bend

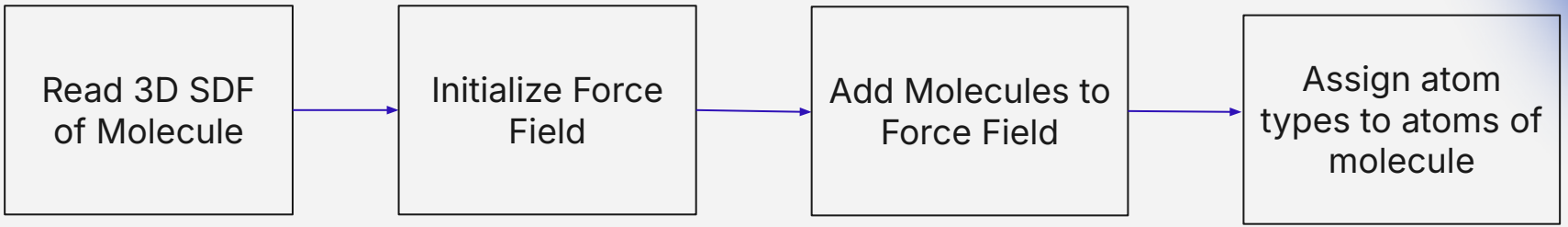


$$\frac{1}{2}ka_{ijk}(\theta - \theta_{eq})$$

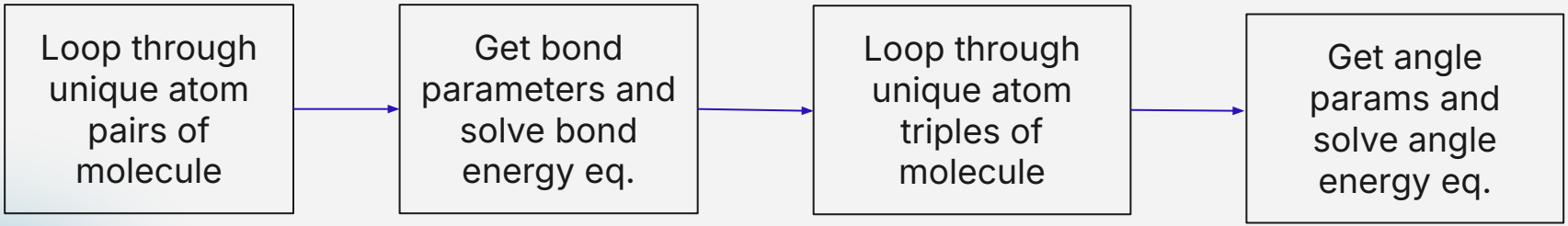
...

Our Implementation

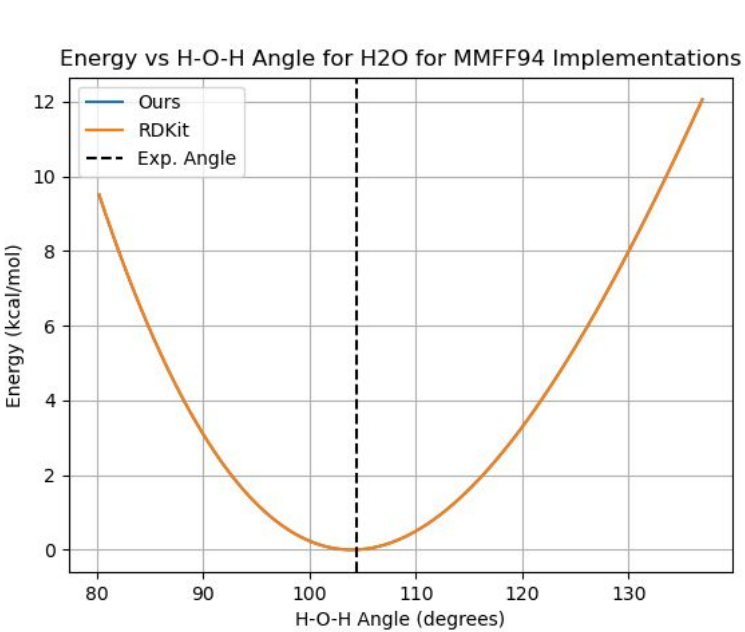
Set-up

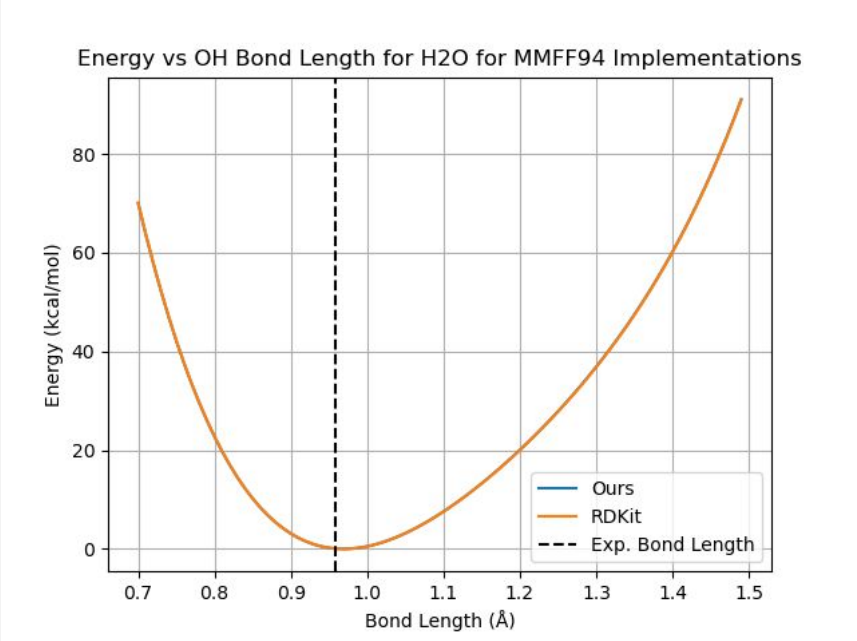


Energy Calc



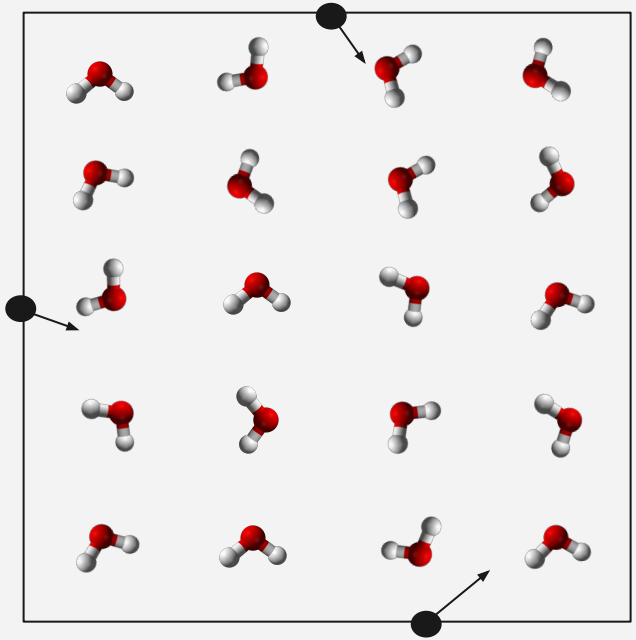
Implementation Comparison





Pivoting

- Initial goal required more complex Force Field than anticipated
- Scrapped potential Molecular Dynamics simulation with Force Field
- Monte Carlo simulation not necessary



03 Calculating Reaction Rates

$$R = \Phi\Sigma = \Phi N\sigma$$

Where:

- Φ, neutron flux $\left(\frac{n}{\text{cm}^2\,\text{s}}\right)$
- Σ, macroscopic cross section (cm^{-1})
- N, atom density $\left(\frac{\text{atoms}}{\text{cm}^3}\right)$
- σ, microscopic cross section (cm^2)

Assume 10^{14} (neutrons/ $\text{cm}^2 \cdot \text{s}$)

$$N = \frac{\rho N_A}{M}$$

Where:

- ρ, density
- N_A, Avogadro's constant
- M, Molecular weight

Typical core parameters:

$$P_{avg} = 2250\ psi$$
$$T_{avg} = 310.5\ ^\circ C$$

Steam Tables

$$\rho = 593.71617\ \frac{kg}{m^3}$$

$$N_{H2O} = (593.71617\ \frac{kg}{m^3})(\frac{1\ m^3}{10^6 cm^3})(\frac{1000\ g}{1\ kg})(6.022 \times 10^{23}\ \frac{atoms}{mol})(\frac{1\ mol}{18.016\ g})$$
$$= 1.98 \times 10^{22}\ \frac{molecules}{cm^3}$$

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$$\sigma_{H2O} \approx 2\sigma_H + \sigma_O$$

$$\sigma_H = (\sigma_H^{tot})_{TH} + (\sigma_H^{tot})_F$$
$$\sigma_O = (\sigma_O^{tot})_{TH} + (\sigma_O^{tot})_F$$

	^1H	^{16}O
Thermal	30.4009 *barn*	2.90842 *barn*
Fast	3.79407384 *barn*	1.57964310 *barn*

$$\sigma_{H2O} = 71.992357 barns$$

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$$R = (10^{14}\ \frac{n}{cm^2 s})(1.98 \times 10^{22} \frac{molecules}{cm^3})(71.992357 \times 10^{-24} cm^2)$$
$$= 142.54 \times 10^{12}\ \frac{reactions}{s}$$

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04 Scaling The Simulation

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Typical core parameters:

$P_{avg} = 2250\ psi$
$T_{avg} = 310.5\ °C$
$Length = 4.17\ m$
$Diameter = 3.37\ m$

assume a metal-to-water ratio of 1:3

$24.55\ m^3$

$4.87 \times 10^{29}\ molecules$

(In the reactor core)

04 Scaling The Simulation

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Scaling factor

$$S_f = \frac{N_{sim}}{N_{core}}$$
$$= \frac{10^{18}}{4.87 \times 10^{29}}$$
$$= 2.05 \times 10^{-12}$$

Applying this scaling factor to the reaction rate we obtain:

$$R_{scaled} = 292.21\ \frac{reactions}{s}$$

05 Determining the Number of Atomic Interactions

- ^1H is simply a proton. A proton has no excited states, and therefore inelastic scattering cannot occur.
- ^{16}O inelastic scattering is possible, but the threshold is $\sim 6\ MeV$, so we will ignore it for simplicity.
- ^1H and ^{16}O cannot undergo fission.

		Thermal	Fast
σ_{se}	^1H	30.0683	1.57964310
	^{16}O	3.79390400	1.5796140
σ_c	^1H	3.325842×10^{-1}	3.687541×10^{-5}
	^{16}O	1.698355×10^{-4}	2.91×10^{-5}

$$\sigma^{se}_{H2O} = 71.326898\ barns$$

$$R_{se} = R_{scaled}\left(\frac{\sigma^{se}_{H2O}}{\sigma^{tot}_{H2O}}\right) = 289.50$$

$$R_c = R_{scaled} - R_{se} = 2.71$$

05 Determining the Number of Atomic Interactions

Recall,

$$\sigma_H = (\sigma_H^{tot})_{TH} + (\sigma_H^{tot})_F$$
$$\sigma_O = (\sigma_O^{tot})_{TH} + (\sigma_O^{tot})_F$$

The number of elastic scattering neutron interactions with Hydrogen per second, R_{se}^H, can be calculated using proportions:

$$\begin{aligned} R_{se}^H &= \frac{2R_{se}((\sigma_H^{tot})_{TH} + (\sigma_H^{tot})_F)}{\sigma_{H2O}^{tot}} \\ &= 267.69 \\ &\approx 268 \end{aligned}$$

We can calculate the number of elastic scattering neutron interactions per second, R_{se}^O, with Oxygen by deduction:

$$\begin{aligned} R_{se}^O &= R_{se} - R_{se}^H \\ &= 21.81 \\ &\approx 22 \end{aligned}$$

06

Sampling Neutron Energies

To obtain neutron energies for the simulation we will perform numerical cumulative distribution function (CDF) sampling using the following method:

- Numerically integrate $\chi(E)$ to obtain the CDF.
- Normalize the CDF between 0 and 1.
- Generate a random number uniformly between zero and one.
- Interpolate the CDF at the random number to find the neutron energy.

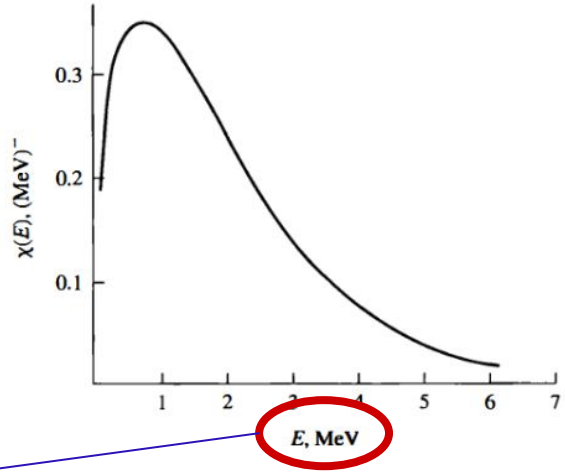

Figure 1: Prompt neutron spectrum

$$\chi(E) = 0.453e^{-1.036E} sinh\sqrt{2.29E}$$

Where, E is the neutron energy in MeV.

We are sampling neutron energies on the order of 10^6 eV! But the O-H bond strength in water is only 5 eV!

07

Calculating the Energy Imparted unto the Target Molecule

Sampled neutron energy
Scattering angle

$$E' = \frac{E_0}{(A+1)^2}[cos\theta + \sqrt{A^2 + sin^2\theta}]^2$$

$$E_{recoil} = E_0 - E'$$

To obtain the scattering angle, the ENDF database contains angular distributions of neutrons based on their energy. The angular distributions are expressed as a normalized probability distribution according to:

$$\int_{-1}^{1} f(\mu, E)d\mu = 1$$

Where $f(\mu, E)d\mu$ is the probability that a particle of incident energy E will be scattered into the interval $d\mu$ about an angle whose cosine is μ. The units of $f(\mu, E)$ are $(unit - cosine)^{-1}$. The distribution is represented as a Legendre polynomial series:

$$f(\mu, E) = \sum_{l=0}^{NL} \frac{2l+1}{2} a_l(E)\ P_l(\mu) \qquad (9)$$

Where:

- l order of the Legendre polynomial
- a_l the l^{th} Legendre polynomial coefficient; it is implicitly understood that $a_0 = 1$
- $P_l(\mu)$ Legendre polynomial of degree l

Perform rejection sampling over the normalized pdf

07

Calculating the Energy Imparted unto the Target Molecule

In order to accurately sample the angular PDF, rejection sampling was performed using the following method:

- The maximum value of $f(\mu, E)$ is computed.
- Two sets of random numbers are generated: the first representing μ on the domain $\{-1, 1\}$, the second representing the random sample y on the domain $\{0, f_{max}\}$
- μ and y are both sampled and the value $f(\mu, E)$ is computed.
- If the sample y is less than the computed value of $f(\mu, E)$, the scattering angle is returned in radians.

08 Molecular Force Field Model

$$E_{recoil} = E_0 - E'$$

We are sampling neutron energies on the order of 10^6 eV! But the O-H bond strength in water is only 5 eV! 🚩🚩🚩🚩

We must make some assumptions about our force field model to scale the recoil energy:

- The three primary components of a molecular force field are the rotational, translational, and vibrational energies.
- The rotational and translational energies are assumed to be classical kinetic energies related to the mass of the molecule.
- The vibrational energy is assumed to be molecular bond energy modeled using classical molecular mechanics.
- The percentage of the recoil energy imparted unto the target molecule responsible for the vibrational energy is proportional to the mass of the interacting molecules.

08 Molecular Force Field Model

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We are sampling neutron energies on the order of 10^6 eV! But the O-H bond strength in water is only 5 eV! 🚩🚩🚩🚩

$$\eta_n = \frac{m_{H2O} - \frac{m_{H2O}}{m_n}}{m_{H2O}} = \frac{m_{H2O}(1 - \frac{1}{m_n})}{m_{H2O}} = 1 - \frac{1}{m_n}$$

$$\eta_n = (1 - \frac{1}{1.0086649})(\frac{1}{100}) = 8.59 \times 10^{-5}$$

$$\Delta(E)_{vib} = \eta_n \ E_{recoil}$$

The rest of the 99.9914% of the recoil energy is transferred into rotational and translational components of the molecule. This energy is ignored because we are assuming that rotational and translational energy does not affect the chemical bonds and therefore does not contribute to molecular decomposition.

Energy imparted unto the target molecule is now scaled to the magnitude of 10^1 eV!

09

Modeling Molecular Decomposition

Vertical Ionization Energy → Energy absorbed in the **GROUND STATE** before ionizing **WITHOUT NUCLEAR REARRANGEMENT.**

Appearance Energy → Amount of energy supplied to a molecule to produce a specific ion.

The NIST Chemistry WebBook for water provides the following appearance energy determinations:

Product Ions	E_{app} (eV)
$H^+ + OH^-$	16 ± 0.3
$H^+ + OH$	16.95 ± 0.05
$HO^+ + H$	18.08 ± 0.05
$O^+ + H_2$	19.0 ± 0.2
$O^+ + 2H$	26.5 ± 0.3

09

Modeling Molecular Decomposition

Model molecular decomposition using the energy well theory, which can be described as:

- Vibrational excitation: The molecule climbs to a higher step in the same well (same geometry, same bonding, more internal motion).
- Electronic excitation: The system is in a new energy well with a different shape (geometry and bond stiffness change).
- Decomposition: Occurs when energy is high enough for the system to escape the well (bond breaking).

The vibrational excitation energy threshold to cause molecular decomposition after ionization is equal to the difference between appearance energy and ionization energy.

This is written in equation form as:

$$(E_{vib})_{crit} = E_{appearance} - E_{ionization}$$

09

Modeling Molecular Decomposition

An interesting observation based on this theory is made by comparing research performed by Rubio titled *Excited States of the Water Molecule* in *The Journal of Chemical Physics*:

Excitation State	$\Delta E_{excitation}(eV)$
$1\ ^1B_1$	7.90
$1\ ^1A_2$	9.11
$2\ ^1A_1$	11.21
$2\ ^1B_1$	13.00
$3\ ^1B_1$	13.19
$3\ ^1A_1$	13.22
$2\ ^1A_2$	13.43

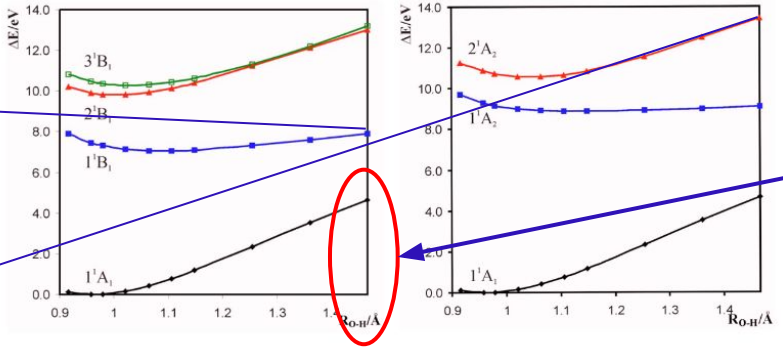

Figure 2: Potential energy curves for excited states of water

$$E_{bond} = \frac{1}{2} k_{bond}(r_{O-H} - r_{eq})^2$$
$$\approx 2.43\ eV$$

Observe in Figure 2 that the potential energy for water in the ground state (1A1) is ~4.8 eV, which is twice the bond energy of a single O-H bond in water.

09

Modeling Molecular Decomposition

We can extend this observation to the rest of the excitation energies determined by Rubio by halving them. Additionally, By using equation (13) and an assumed ionization of 12.6 eV, we can tabulate the critical vibrational excitation energies to form specific ions:

Excitation State	$(E_{bond})_{O-H}$ (eV)
$1\ ^1B_1$	3.95
$1\ ^1A_2$	4.555
$2\ ^1A_1$	5.605
$2\ ^1B_1$	6.5
$3\ ^1B_1$	6.595
$3\ ^1A_1$	6.61
$2\ ^1A_2$	6.715

Bond energies ($r_{O-H} = 1.4568\mathring{A}$) for a single O-H bond in water

Product Ions	$(E_{vib})_{crit}$ (eV)
$H^+ + OH^-$	3.4 ± 0.3
$H^+ + OH$	4.35 ± 0.05
$HO^+ + H$	5.48 ± 0.05
$O^+ + H_2$	6.4 ± 0.2
$O^+ + 2H$	13.9 ± 0.3

Critical vibrational excitation energies to form specific ions

10

Estimating Radiolytic Decomposition of Water

WE DON'T EVEN NEED A FORCE FIELD MODEL! If the energy imparted unto the incident molecule is greater than the minimum appearance energy we can assume the molecule instantaneously decomposes.

$$R_{se}^{H} = \frac{2R_{se}((\sigma_H^{tot})_{TH} + (\sigma_H^{tot})_F)}{\sigma_{H2O}^{tot}}$$
$$= 267.69$$
$$\approx 268$$

86400 seconds in one day

Sample $268 * 86400$ neutron energies for hydrogen interactions

$$R_{se}^{O} = R_{se} - R_{se}^{H}$$
$$= 21.81$$
$$\approx 22$$

Sample $22 * 86400$ neutron energies for oxygen interactions

Take the proportion of energies greater than 16 eV as the number of interactions which caused molecular decomposition.

10 Estimating Radiolytic Decomposition of Water

Instead of taking 290 * 86400 ~ 25e6 samples, we estimated the result by taking 10,000 samples and generalizing the result:

Applying the simulation scaling factor we obtain: 8.83e18 decompositions at 100% power in 24 hours. This converts to 6.97e-8 gallons.

$$4.87 \times 10^{29}(molecules)(2.927 \times 10^{-16}(\frac{interactions}{second}))(0.722(\frac{decompositions}{interaction}))(86400(\frac{seconds}{hour}))$$
$$= 8.89 \times 10^{18} decompositions$$

Recall, the total reaction rate was 142.54e12 reactions per second and there are 4.87e29 molecules in the core. Meaning 2.93e-14% of water molecules experience a neutron interaction every second.

However, of the neutron-water molecule interactions which do occur, this results in 72.2% probability that a single neutron-water molecule interaction causes a decomposition.

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Water will decompose upon interacting with the prompt neutron: 72.2759 percent of the time
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(Proof that I actually got that result)

USS Key West SSN-722

Biggest Conch in the Pacific