Density Functional Theory Study on the Activation of Molecular Oxygen on Stepped Gold Surface in Aqueous Environment: A New Approach for Simulating Reactions in Solution

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1. Theory of free energy calculation at liquid-solid interface

The calculation of free energy at liquid-solid interface in this work mainly follows the general scheme derived by Trhular et al.[1, 2] for liquid solution. The details are briefly summarized as follows.

Based on the Born-Oppenheimer approximation and the ground state, the free energy $G(S)$ in arrangement S follows[3]

$$e^{-\beta G(S)} = C \int_S dRdPdrdp e^{-\beta H(R,P,r,p)} \tag{s1}$$

where C is a constant depending on the standard state, H is the Hamiltonian, and β is $1/k_B T$ where k_B is Boltzmann's constant and T is temperature. R, P, r and p denote the $3N$-6 internal coordinates of the solute ($3N$-7 internal coordinates of the linear solute molecule), conjugate momenta of solute, the remaining coordinates and conjugate

momenta of the entire system (solute plus solvent), respectively.

The integration of eq. s1 can be performed in two steps:

$$e^{-\beta W(R(S))} = C' \int dR' dP dr dp \delta(R - R') e^{-\beta H(R',P,r,p)} \tag{s2}$$

$$e^{-\beta G(S)} = C'' \int_S dR e^{-\beta W(R(S))} \tag{s3}$$

where C' and C'' are constants again depending on the standard state, W is the free energy surface (FES) or potential of mean force (PMF) including the internal energy of the solute in solution, namely the liquid-phase expectation value of the gas-phase Hamiltonian, $E(R_l)$, and the coupling free energy of the rigid solute to the solvent at structure point R, $\Delta G_{coup}(R_l)$,

$$W(R_l) = E(R_l) + \Delta G_{coup}(R_l) \tag{s4}$$

In terms of Ben-Naim's statistical thermodynamic interpretation of the solvation process[4], μ_i, the chemical potential of species i in a liquid-phase solution follows

$$\mu_i = \mu_i^* + TS_{lib,i} \tag{s5}$$

where μ_i^* is the chemical potential of a species whose center of mass is constrained to a fixed position in the solution, and $S_{lib,i}$ is the entropy of liberation species i. μ_i^* is composed of the internal free energy of the species i in solution and its coupling to the solvent. Hence, the system $G(S)$ is given by

$$G(S) = \sum_{i=1}^{n(S)} N_i(S)\mu_i(S) = U_0(S) + G_{int}(S) + TS_{lib}(S) \tag{s6}$$

where $n(S)$ is the number of all the species in arrangement S, $G_{int}(S)$ is the internal thermal free energy including electronic-vibrational-rotational and conformational free energy, and $U_0(S)$ is the FES including zero-point-energy correction, namely

$$U_0(S) = W(R(S)) + \frac{1}{2}hc \sum_{n=1}^{I(R_l(S))} \omega_n(S)$$

$$= E(R_i(S)) + \Delta G_{coup}(R_l(S)) + \frac{1}{2}hc \sum_{n=1}^{I(R_l(S))} \omega_n(S)$$

(s7)

where $I(S)$ is the internal coordinates of all species,

$$I(S) = \sum_{i=1}^{n(S)}[3N_i(S) - 6]$$

(s8)

for local minima and

$$I(S) = \sum_{i=1}^{n(S)}[3N_i(S) - 7]$$

(s9)

for transition state.

For $\Delta G_{coup}(R_l)$, it includes two parts: I. The internal energy contribution, $\Delta E_{coup}(R_l)$, involves hydrophobic effects, hydrogen bonding, dispersion, exchange repulsion between solute and solvent and the internal energy change of solvent rising from the cavitation and reorganization of solvent structure effects; II. The change of internal free energy of solvent molecules, $\Delta G_{coup\text{-}int}(R_l)$, involves hindered rotational, vibrational and conformational change rising from hydrophobic effect, the cavitation and reorganization of solvent structure effect with the introduction of solute. For the conformational change, it has been demonstrated that it is tightly related to the flexibility and the volume of solute [4,5]. The conformational change $\Delta G_{conf}(R_l)$ follows

$$\Delta G_{conf}(R_l) = -nRTlnZ^x$$

(s10)

where x is the number of points of flexibility per molecule, Z is the number of possible orientations change of equal energy at each such point, and n is the number of the adjacent solvent molecule influenced from the formation of cavitation for one solute molecule. For example, when one mole O_2 enters aqueous solution at ambient

temperature, $Z=2$, $x=1$, and $n=1.77$. So $\Delta G_{conf}(R_l) = 1.77RTln2 = 0.03$ eV. This low value indicates that the conformational free energy contribution can be truncated for the reaction between small solute with low flexibility.

Hence for the small solute with low flexibility, $G(S)$ can be given by

$$G(S) = E(r_l(S)) + \frac{1}{2}hc\sum_{n=1}^{I(r_l(S))}\omega_n(S) + G_{rotvib}(r_l(S)) + TS_{lib}(S) - G'_{solvent} \qquad (s11)$$

in which $E(r_l(S)) + \frac{1}{2}hc\sum_{n=1}^{I(r_l(S))}\omega_n(S)$ is the internal energy of solution with zero-point-correction, $G_{rotvib}(r_l(S))$ is the sum of hindered rotational and vibrational contribution for solution, and $G'_{solvent}$ is the initial free energy of solvent in the absence of solute without conformational contribution. Hence the free energy variation of elementary reaction for small solute at the standard state in the solution follows

$$\Delta G^o(S) = \Delta E(r_l(S)) + \Delta(\frac{1}{2}hc\sum_{n=1}^{I(r_l(S))}\omega_n(S)) + \Delta G^o_{rotvib}(r_l(S)) + T\Delta S^o_{lib}(S) \qquad (s12)$$

Especially for the reaction occurring at liquid-solid interface, the liberation free energy equals zero, and the hindered rotational contribution of intermediate in liquid solution further becomes frustrated vibrational contribution. Therefore for the reaction of small molecule with low flexibility at liquid-solid interface, the free energy change of the elementary step without considering solid lattice vibrational coupling obeys

$$\Delta G^o(S) = \Delta E(r_{l-s}(S)) + \Delta(\frac{1}{2}hc\sum_{n=1}^{3N}\omega_n(S)) + \Delta G^o_{vib}(r_{l-s}(S))$$

where N is the number of atoms at liquid-solid surface including the intermediates and solvent molecules.

In our calculations, the quasi-harmonic approximation was utilized to identify

the vibrational frequencies, which is the same as the usual harmonic oscillator approximation except that vibrational frequencies lower than 100 cm^{-1} were raised to 100 cm^{-1} as a way to correct for the well-known breakdown of the harmonic oscillator model for the free energies of low-frequency vibrational modes. The accuracy of this method has been demonstrated by previous work[1, 2, 6].

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