Theoretical study on isotope fractionation of uranium crystal produced in abiotic reduction

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During the biotic reduction of hexavalent uranium (U(VI)) to tetravalent uranium (U(IV)) mediated by bacteria, the heavier isotope ($^{238}$U) is enriched in U(IV), but the abiotic reduction mediated by abiotic reductants does not show the same trend of isotope fractionation.1 Hence, uranium isotope may give an insight into ancient microbial activity. However, the reason of this difference has not been uncovered yet. In this study, we focused on the abiotic reduction and calculated the isotope fractionation coefficient $\varepsilon$ between $\text{UO}_4^2-(CO_3)_3^4-$ and uraninite ($\text{UO}_2$) crystal, the reactant and product of the abiotic reduction, respectively, assuming equilibrium.

$\varepsilon$ can be approximated as the sum of the nuclear mass term $\ln K_{nm}$ and the nuclear volume term $\ln K_{nv}$.2 We calculated $\ln K_{nm}$ by obtaining the harmonic frequencies using VASP5.4.1. On the other hand, $\ln K_{nv}$ is highly affected by relativity significant because the electronic state around the nucleus is important.3 However, computational method assuming periodic boundary condition (PBC) with relativistic effect has not been established. Thus, we used the method for calculating $\ln K_{nv}$ from the calibration curve between the electron density at the nucleus ($\rho(0)$) obtained by PBC and relativistic calculations.4 In our calculations, we used ABINIT8.8.3 for the PBC calculation and DIRAC16 for the relativistic calculation and calculated $\rho(0)$ for 25 isolated molecules shown in Fig. 1. Figure 1. Relationship between $\rho(0)$ obtained by ABINIT8.8.3 and DIRAC16.