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Molecular dynamics simulation of local structure and vibrational spectrum of uranyl $(UO_2)^{2+}$ in vitreous B_2O_3

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Laser spectroscopic and extended X-ray absorption fine structure (EXAFS) spectra have shown that uranium in B_2O_3 glass matrix forms uranyl in the electronic configuration of $(UO_2)^{2+}$, but its surrounding structure is not well known. Understanding of uranyl local structure, ion-ligand interaction, and chemical stability on the nanometer scale in glasses is essential in management of long-term performance of high-level nuclear wastes after disposal in a geologic repository. In the present work, the structure, phonon density of states, and vibrational spectrum of vitreous B_2O_3 and the surrounding environment that contains a uranyl ion have been studied using a molecular dynamics (MD) simulation method that utilizes the Born-Mayer-Huggins and Coulomb pair potentials and the Stillinger-Weber three-body potential. A system of 406 ions was considered in our calculation. Simulation of a thermal quenching from 3000 K to 300 K was performed to generate a uniform and equilibrium model glass matrix before structure configuration and vibrational frequencies were obtained from the system. The structure of the simulated glass is in agreement with that reported by Krogh-Moe [1] and Mozzi et al. [2] The characteristic network of planar boroxol (B_3O_6) rings is evident in the simulated system. [3] A configuration of a U^{6+} cation in the vitreous B_2O_3 matrix is shown in Fig.1. It is shown that a nearly linear $(UO_2)^{2+}$ uranyl ion is coordinated by four equatorial oxygen anions in an approximately planar arrangement. The U-O bond length is approximately 0.178 nm for the axial oxygen and 0.254 nm for the equatorial oxygen, which is in good agreement with the U-O distances obtained from fitting EXAFS spectra. Based on the simulated model structure, the uranyl vibrational spectrum is simulated and compared with experimental results obtained using site-selective fluorescence line narrowing (FLN) techniques.

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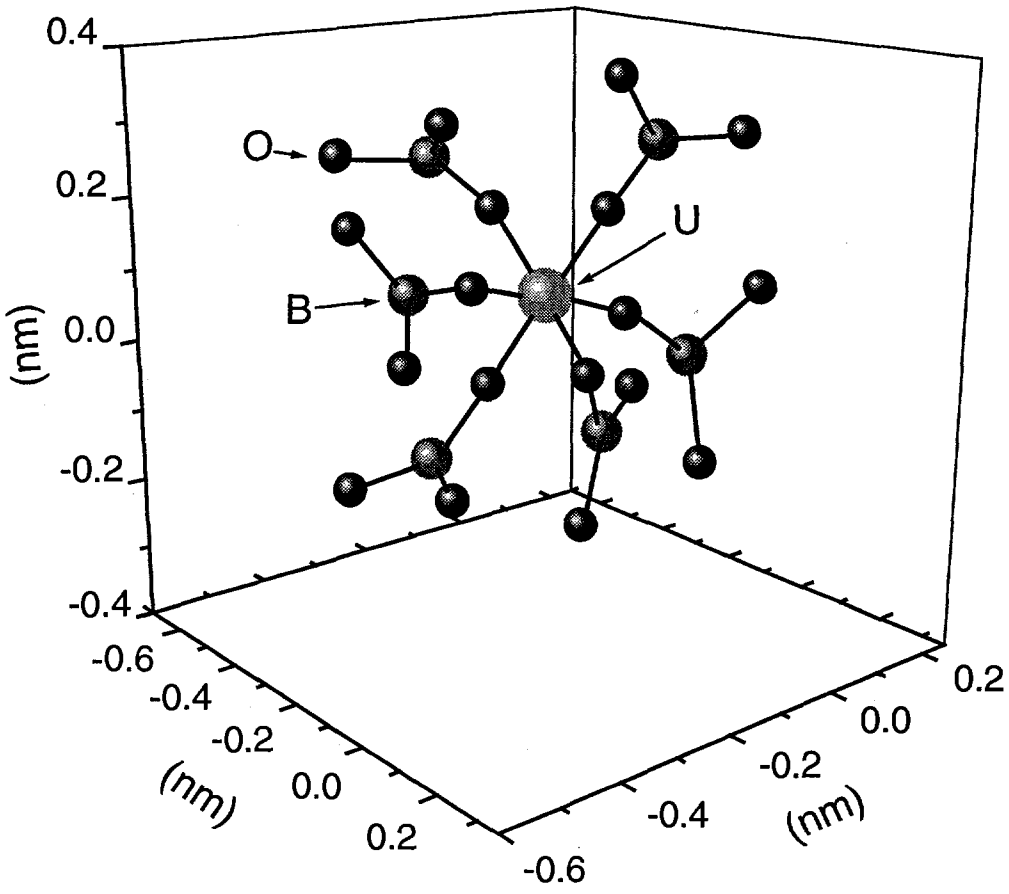

Fig. 1 Simulated local structure for uranyl in B_2O_3 glass matrix.

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