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Atomic Scale Force Spectroscopy Suggests Low Reorganization Entropy For Electron Transfer J.T. SAGE, A. BARABANSCHIKOV, B. BARBIELLINI, Northeastern Univ., E.D. COULTER, D.M. KURTZ, Univ. Georgia, E.E. ALP, W. STURHAHN, Argonne Natl. Lab — Molecular mechanics simulations of the electron transfer protein rubredoxin suggest significant delocalization of active site vibrations, but experimental vibrational data have been successfully modelled using empirical models that exclude distant atoms. We address this question using nuclear resonance vibrational spectroscopy (NRVS), an emerging synchrotron-based technique that yields the complete vibrational spectrum of ^{57}Fe in rubredoxin, coupled with quantum chemical vibrational predictions. The measured vibrational density of states reveals that oxidation strengthens the Fe-S bonds linking iron to the polypeptide, as expected from the reported decrease in Fe-S bond lengths. Moreover, comparison with Raman isotope shift measurements provides direct experimental evidence that the Fe-S vibrations remain localized at the active site. Vibrational predictions based on DFT calculations reproduce the observed vibrational data and confirm the localized nature of the Fe-S vibrations, although lower frequency vibrations mix significantly with the polypeptide. The Fe-S vibrations are an important component of the electron transfer reaction coordinate, and we suggest that vibrational localization may facilitate electron transfer by minimizing the reorganization entropy of the reaction.

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