Ribonuclease A (RNase A) is immobilized on silver surfaces in oriented and random form via self-assembled monolayers (SAMs) of alkanethiols [1]. The immobilization process is characterized step-by-step using chemically-selective near-edge x-ray absorption fine structure spectroscopy (NEXAFS) at the C, N, and S K-edges. The orientation of the protein layer manifests itself in an 18% polarization dependence of the NEXAFS signal from the N 1s to π* transition of the peptide bond, which is not seen for a random orientation (Fig. 1). The S 1s to C−S σ* transition exhibits an even larger polarization dependence of 41%, which is reduced to 5% for a random orientation. A quantitative model is developed for calculating the polarization dependence, which explains both the sign and the magnitude of the observed intensity modulation at both edges [2].

These results suggest that NEXAFS can be used to investigate fairly complex organic molecules immobilized on a surface, such as proteins containing more than one hundred amino acid residues. Such element-specific, surface-sensitive diagnostics can facilitate the development of a fuller understanding of processes occurring at interfaces that support proteins.

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