Vibrational Spectroscopy of N_3^- in the Gas and Condensed Phase

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Abstract

Azido-derivatized amino acids are potentially useful, positionally resolved spectroscopic probes for studying the structural dynamics of proteins and macromolecules in solution. To this end a computational model for the vibrational modes of N_3^- based on accurate electronic structure calculations and a reproducing kernel Hilbert space representation[1,2] of the potential energy surface for the internal degrees of freedom is developed. Fully dimensional quantum bound state calculations[3] find the antisymmetric stretch vibration at 1974 cm^{-1} compared with 1986 cm^{-1} from experiment.[4,5] This mode shifts by 64 cm^{-1} (from the frequency distribution) and 74 cm^{-1} (from the IR lineshape) to the blue, respectively, compared with 61 cm^{-1} from experiment for N_3^- in water.[6] The decay time of the frequency fluctuation correlation function is 1.1 ps, in good agreement with experiment (1.2 to 1.3 ps)[7,8] and the full width at half maximum of the asymmetric stretch in solution is 18.5 cm^{-1} compared with 25.2 cm^{-1} from experiment.[6] A computationally more efficient analysis based on instantaneous normal modes is shown to provide comparable, albeit somewhat less quantitative results compared to solving the 3-dimensional Schrödinger equation for the fundamental vibrations. This model for N_3^- is then also used to characterize the dynamics around

hydrated azidohomoalanine, an experimentally relevant modification of alanine residues to investigate protein dynamics in solution.[9]

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