

PROBING THE CONFORMATIONAL LANDSCAPE AND THERMOCHEMISTRY OF DINUCLEOTIDE ANIONS VIA HELIUM NANODROPLET INFRARED ACTION SPECTROSCOPY

DANIEL A THOMAS^a, RAYOON CHANG, EIKE MUCHA, MAIKE LETTOW, KIM GREIS, GERARD MEIJER, GERT VON HELDEN, *Department of Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany.*

When molecules are captured in a helium nanodroplet, the rate of cooling to an equilibrium temperature of ca. 0.4 K is faster than the rate of isomerization, resulting in “shock-freezing” that kinetically traps molecules in the local conformational minimum. This unique property enables the study of temperature-dependent conformational equilibria via infrared spectroscopy without the deleterious effects of spectral broadening at higher temperatures.^{b,c} We utilize this approach to explore the equilibrium conformer populations of deprotonated dinucleotides, which have been shown previously by ion mobility spectrometry to exhibit a strong temperature dependence.^d Dinucleotide anion species were generated by electrospray ionization, confined in a helium-buffer-gas ion trap at temperatures between 90 and 350 K, and entrained in traversing helium nanodroplets. The infrared spectra of the dinucleotide ions captured in nanodroplets show a strong dependence on pre-pickup ion temperature, consistent with the preservation of conformer populations prior to cooling in the helium nanodroplet. Non-negative matrix factorization was utilized to identify component conformer infrared spectra and thereby determine temperature-dependent conformer populations. Relative enthalpies and entropies of conformers were subsequently obtained from a van 't Hoff analysis. These initial results demonstrate the promise of this technique to elucidate competing intramolecular interactions and experimentally measure thermochemical parameters for isolated biomolecular ions.^e

^aPresent Address: University of Rhode Island, Department of Chemistry, Kingston, RI 02881

^bD. S. Skvortsov, A. F. Vilesov, *J. Chem. Phys.* **2009**, *130*, 151101.

^cC. M. Leavitt *et al.*, *J. Phys. Chem. A* **2014**, *118*, 9692-9700.

^dJ. Gidden, M. T. Bowers, *Eur. Phys. J. D* **2002**, *20*, 409-419.

^eD. A. Thomas *et al.*, *Phys. Chem. Chem. Phys.* **2020**, *22*, 18400-18413.