National Aeronautics and Space Administration

FY23 Strategic University Research Partnership (SURP)

Unambiguous Detection of Biosignatures by Action Spectroscopy

Principal Investigator: Frank Maiwald (3801); **Co-Investigators:** Robert Hodyss (3220), Mathias Weber (University of Boulder), Lane Terry (University of Boulder)

Objectives: The primary objective was to demonstrate the advantages of messenger photodissociation action spectroscopy for the detection of biomarkers in the presence of their structural isomers. Our collaboration with CoI Weber's team, in particular graduate students Lane Terry and Maddie Klumb, enabled this investigation with an active apparatus (Fig. 1) that includes electrospray ionization, a cryogenic quadrupole trap (temperature control from 10 to 300 K), and coherent radiation sources spanning the mid-infrared, visible, and ultraviolet (ca. 15 μm up to 220 nm).

Background: Accurate identification and quantification of biomarkers, which may be found in the presence of a complex mixture of molecules and their isomers, is crucial for future life detection (Table 1). Action spectroscopy provides a simple implementation with existing mass spectrometers, using an electrospray ionization (ESI) source coupled to an ion trap-based mass analyzer that is equipped with infrared laser channels capable of dissociating messenger molecules (ex. N_2:20-35 K, O_2:25-40 K, CH_4:45-65 K, and H_2O:165-185 K) that are weakly coupled to a charged biomarker.

Approach and Results: Employing messenger-tagging to measure vibrational spectra of mass-selected ions, target ions are prepared as protonated cations (MH^+) or as deprotonated anions ($M\text{-}H)^-$ are generated by ESI and transferred through ion-guides into a temperature controlled Paul trap (10-300 K), where they collision-cool with buffer-gas (He or D_2). During cooling, trapped ions can form complexes with small molecules ("messenger-tags", T) contained in the buffer-gas. After this step, complexes $MH^+ \cdot T$ are formed, mass-selected, and irradiated with a tunable, nanosecond-pulsed infrared (IR) OPO/OPA (700-4500 cm^{-1}, $\Delta\omega$<5 cm^{-1}, $E_{pulse} \approx$ 50-400 μJ). If the complexes absorb photons on a vibrational transition, they can undergo unimolecular decomposition according to the reaction: $MH^+ \cdot T + \hbar\omega_{IR} \rightarrow MH^+ + T$. This process is detected by observation of fragment ions MH^+ in a second mass spectrometer. Recording the intensity of fragment ions as a function of the IR photon energy yields the vibrational spectrum of the complex, weighted by the quantum yield for dissociation for each transition. We successfully prepared protonated valine ions ($ValH^+$) by ESI (0.1mM concentration, 1:1 methanol:H_2O), detected the formation of N_2 adducts ($ValH^+ \cdot N_2$) at cryogenic temperatures (35K), and employed photodissociation (Fig. 2). Similar experiments on deprotonated valine, $[Val\text{-}H]^-$, and deprotonated aminovaleric acid (an isomer with the same atomic composition and similar functional groups) revealed different IR signatures (Fig. 3), confirming that infrared photodissociation action spectroscopy can distinguish selected biomarkers from other molecules with the same mass and atomic composition. Accompanying density functional theory calculations (DFT, B3LYP functional, cc-pVTZ basis) allow identification of the *trans* conformer family for $ValH^+$ (Fig. 2), based on its lower energy and its overall fit with the experimental spectrum. The most intense line antisymmetric OCO stretching mode, has a calculated intensity of 232 km/mol.
N_2 is the optimal tag tested so far (Table 1) with a calculated binding energy of ca. 1200 cm^{-1}. It is more suitable than H_2O (calc. ca. 5000 cm^{-1}), and attempts to observe photofragment signals with $ValH^+ \cdot H_2O$ complexes in the fingerprint region of the spectrum (1000-2000 cm^{-1}) were unsuccessful so far. The observation of CH_4 adducts is promising, since they occur at a slightly higher temperature than N_2, making CH_4 tags potentially more suitable for the surface temperatures of possible target worlds. In addition, their calculated binding energy (ca. 560cm^{-1}) likely results in a greater photodissociation quantum yield than N_2.

Significance/Benefits to JPL and NASA: This research brings infrared absorption spectroscopy and mass spectrometry together to define a new type of instrument with existing technologies to provide mass and structural information. The partnership with UC Boulder will open up novel, state-of-the-art experimental capabilities for in situ sensing on planetary missions and involves students/postdocs in space applications.

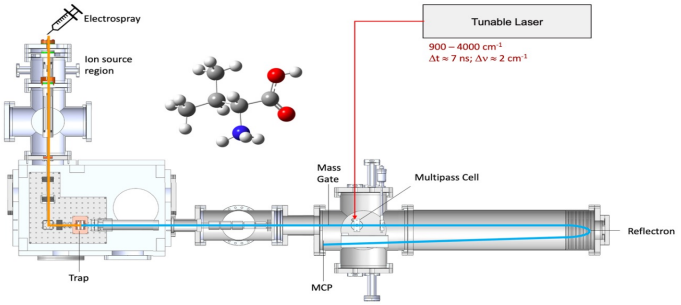

Figure 1. Schematic overview of the cryogenic infrared ion action spectroscopy setup at University of Boulder.

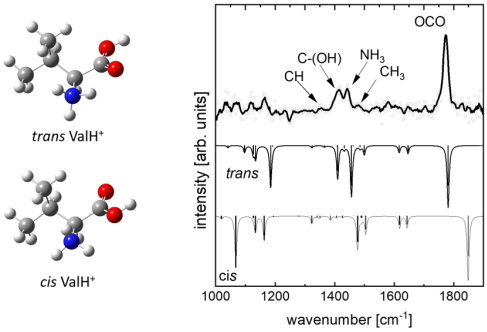

Figure 2. Experimental IR photodissociation spectrum of N_2-tagged, protonated valine, $ValH^+$-N_2 (top, upright) compared to the calculated spectra of the lowest energy structures of the trans and cis structural families of $ValH^+$ (inverted, shown with the same vertical scale).

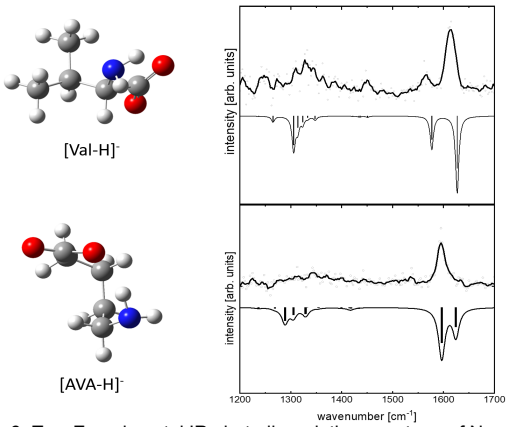

Figure 3. Top: Experimental IR photodissociation spectrum of N_2-tagged, deprotonated valine, $[Val\text{-}H]^- \cdot N_2$ (top, upright) compared to the calculated spectrum of the lowest isomer of $[Val\text{-}H]^-$ (inverted). Bottom: same with deprotonated aminovaleric acid, $[AVA\text{-}H]^- \cdot N_2$. m/z = 118.15 for both.

Table 1. Temperature range of solar bodies of interest.

Target	Temperature range (K)	Target Molecules	Comments	Example Missions
Europa	50-110	amino acids, fatty acids, nucleobases	High radiation environment	Lander
Enceladus	33-145		plume deposition	Orbiter/ Lander
Ceres	110-235		Relic ocean world	Lander/ Sample
Titan	95	aromatics, nitriles, tholins	Complex organic environment	Dragonfly

Publications:

[A] Lane M. Terry, Deacon Nemchick, and J. Mathias Weber, "CRYOGENIC ION SPECTROSCOPY OF VALINE AND CHEMICAL ANALOGS," 76th International Symposium on Molecular Spectroscopy, Urbana/Champaign, IL, June 2023.
[B] Lane M. Terry, Maddie K. Klumb, Deacon J. Nemchick, Robert P. Hodyss, Frank W. Maiwald, and J. Mathias Weber, "Cryogenic Ion Vibrational Spectroscopy of Protonated and Deprotonated Valine and of Deprotonated Aminovaleric Acid" (working title), in preparation for publication.

PI/Task Mgr. Contact Information:

Frank Maiwald, phone:4-0214, Frank.Maiwald@jpl.nasa.gov

National Aeronautics and Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

www.nasa.gov

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