

FY25 Strategic University Research Partnership (SURP)

Unambiguous Detection of Biosignatures by Action Spectroscopy

Principal Investigator: Deacon Nemchick (329)

Co-Investigators: Robert Hodyss (322), Mathias Weber (University of Colorado - Boulder)

Graduate Student Participants: Lane Terry, Maddie Klumb

Objectives: The primary objective of this SURP effort is to demonstrate the advantages of messenger assisted action spectroscopic techniques in the infrared for the unambiguous detection of biomarker molecules including their mass-degenerate structural analogs. These techniques, which can obtain the vibrational spectrum of mass selected ions using ion (not optical) detection, are highly sensitive and could prove valuable for future mass spectrometer-based in situ sensing instrumentation. To advance project objectives, this work invokes the unique experimental capabilities and decades of subject-matter expertise associated with the research group of Professor Mathias Weber at the University of Colorado (Boulder). The SURP work plan heavily leverages the Weber group cryogenic ion apparatus depicted in Figure 1. Experimental trials executed over the course of this effort will help define performance parameters for future planned photodissociation-based in situ sensor platforms which by necessity will have a much narrower operational scope.

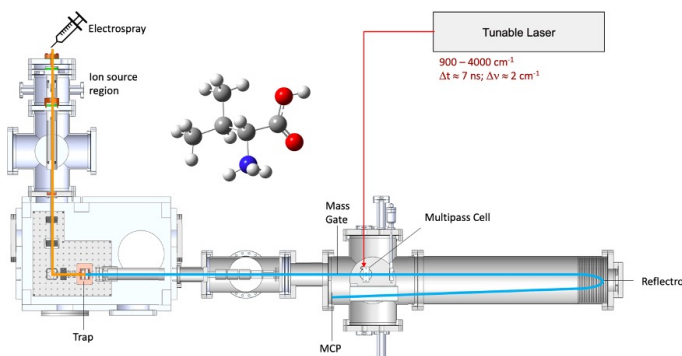


Figure 1: Schematic overview of the cryogenic infrared ion action spectroscopy setup native to the Weber Group at the University of Colorado - Boulder.

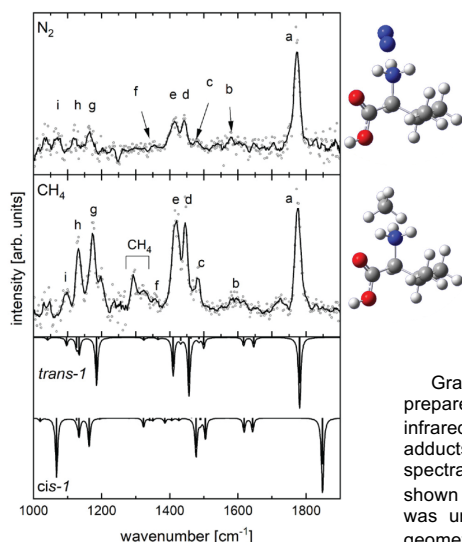


Figure 2: IR photodissociation spectra (upright) of protonated valine collected with two different tagging partners (N₂ top; CH₄ below). Calculated spectra of different structures of ValH⁺ (inverted, shown on the same vertical scale). See <https://doi.org/10.1021/acs.jpca.4c03552>.

Significance/Benefits to JPL and NASA: Adaptation of established photodissociation techniques for use in planetary science in situ sensing applications is an emerging field of development. JPL has a long heritage relating to the build, validation, and delivery of traditional one-dimensional mass analyzers for space applications and can potential serve as a development hub for this new hybrid class of instrument. Concept maturation is critically dependent upon establishing a working relationship with partners having subject matter expertise. Such collaborations also increasing access to students and potential postdoctoral candidates having highly specialized knowledge for a diverse range of mass spectrometry techniques and technologies.

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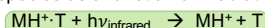
PI/Task Mgr. Contact Information:

Deacon Nemchick (329) o: (818) 354-0322

Deacon.J.Nemchick@jpl.nasa.gov

This project recognizes the late Dr. Frank Maiwald.

Approach and Results: The Boulder team uses a unique cryogenic photodissociation spectrometer (Fig. 1) for collecting the infrared action spectra of biomarker molecules of interest. Target ions are prepared as protonated cationic species, MH⁺, or as deprotonated anionic species, [M-H]⁻ via electrospray ionization. Non-covalent messenger tagged complexes of the form MH⁺·T are formed inside a temperature controlled Paul trap (10-300 K). Infrared spectra can then be recorded by monitoring the formation of the untagged species as a function of irradiation wavelength.



Graduate student participants from the Weber group successfully prepared protonated valine ions (ValH⁺) by ESI and collected the infrared action spectrum of both the nitrogen and methane tagged adducts (ValH⁺·N₂ at 30 K and ValH⁺·CH₄ at 65 K). The resulting spectra and the comparison with density functional calculations are shown in Fig. 2). The results show that the trans conformer family was unambiguously identified as the only significantly populated geometry, based on its lower energy and its overall fit with the experimental spectrum. CH₄ is the optimal tag tested so far. Its binding energy (calculated ca. 970 cm⁻¹) make it more suitable tagging partner than N₂ (ca. 1670 cm⁻¹) or water (ca. 5000 cm⁻¹).

Experiments on deprotonated valine, [Val-H]⁻, and deprotonated aminovaleric acid, [AVA-H]⁻, (an isomer with the same atomic composition) revealed different IR signatures (Fig. 3). This confirms that infrared photodissociation action spectroscopy can distinguish biomarkers from molecules with the same mass and atomic composition. We identified suitable messenger tags and their optimal temperature range. So far CH₄ (60 K) was found to be the optimal tag for ValH⁺. Tagging with O₂ (25 K) produced lower abundances of tagged ions, and H₂O (180 K) showed no IR photofragments. N₂ tags (30 K) require temperatures below typical surface temperatures of target worlds (e.g., Europa, Enceladus).

Publications:

L. M. Terry, M. K. Klumb, D. J. Nemchick, R. Hodyss, F. Maiwald, J. M. Weber, J. Phys. Chem. A 2024, 128, 34, 7137–7144. <https://doi.org/10.1021/acs.jpca.4c03552>.

L. M. Terry, M. K. Klumb, D. J. Nemchick, R. Hodyss, J. M. Weber, J. Phys. Chem. A 2025, 129, 26, 5837–5842. <https://doi.org/10.1021/acs.jpca.5c03141>.

Lane M. Terry, Deacon J. Nemchick, J. Mathias Weber, Cryogenic Ion Spectroscopy of Valine and Chemical Analogs, International Symposium on Molecular Spectroscopy, Contributed Talk, Urbana-Champaign, IL, June 2023.

Maddie K. Klumb, Lane M. Terry, Deacon J. Nemchick, Robert Hodyss, Frank Maiwald, J. Mathias Weber, Cryogenic Ion Vibrational Spectroscopy of Protonated Nicotinamide, International Symposium on Molecular Spectroscopy, Contributed Talk, Urbana-Champaign, IL, June 2024.

Lane M. Terry, Deacon Nemchick, Robert P. Hodyss, Frank Maiwald, and J. Mathias Weber, Cryogenic Ion Vibrational Spectroscopy of Deprotonated Valine and Deprotonated Aminovaleric Acid, International Symposium on Molecular Spectroscopy, Contributed Talk, Urbana-Champaign, IL, June 2024.

Lane M. Terry, Maddie K. Klumb, Deacon Nemchick, Robert Hodyss, Frank Maiwald, and J. Mathias Weber, Exploring Use of Clusters for Unambiguous Detection of Biomarkers on Planetary Missions, Invited Hot Topics Talk, Gordon Research Conference on Molecular Ionic Clusters, Ventura, CA, February 2024

Lane M. Terry, Maddie K. Klumb, Deacon Nemchick, Robert Hodyss, Frank Maiwald, and J. Mathias Weber, Cryogenic Ion Vibrational Spectroscopy of Protonated and Deprotonated Valine and of Deprotonated Aminovaleric Acid, Poster, Gordon Research Conference on Molecular Ionic Clusters, Ventura, CA, February 2024

M. K. Klumb, L. M. Terry, D. J. Nemchick, R. Hodyss, F. Maiwald, J. M. Weber, Messenger Tagging Vibrational Spectroscopy of Protonated Nicotinamide (working title), in preparation for publication (September 2025).

Infrared Action Spectra of Mass Degenerate Compounds

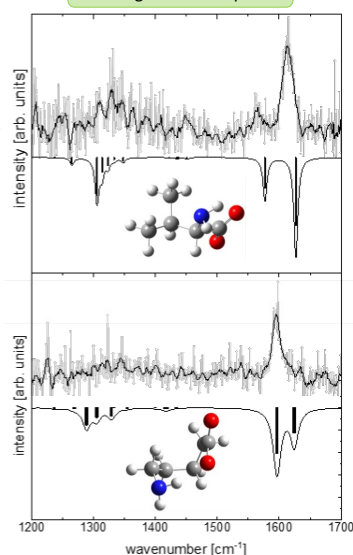


Figure 3: Experimental IR photodissociation spectrum of N₂-tagged, deprotonated valine, [Val-H]⁻·N₂ (top, upright) and constitutional isomer aminovaleric acid, [AVA-H]⁻·N₂ (top, upright). Unique spectral patterns can identify these compounds without the aid of a chromatography stage. Corresponding calculated spectra are inverted.