

Physical Chemistry Seminar

Vibrational Spectral Signatures and Ultrafast Dynamics of Strong H-bonds Investigated with Cryogenic Ion and 2D IR Spectroscopies

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H-bonding interactions and proton transfer processes play central roles throughout chemistry and biology. Spectroscopic studies that directly probe strong H-bonds and proton transfer reactions, however, remain a formidable experimental challenge. We aim to characterize vibrational spectral signatures and dynamics of strong H-bonds by complementing high-resolution gas-phase techniques (cryogenic ion spectroscopy) with ultrafast time-resolved solution-phase experiments (transient absorption, 2D IR). First, we report gas-phase studies on a series of proton-coupled electron transfer (PCET) model systems, which exhibit extremely broad shared H atom stretch transitions. Computational modeling reveals a unique spectral mechanism arising from significant anharmonic coupling of the H atom degrees of freedom to nearly three dozen normal mode coordinates. Next, solution-phase studies investigating the intramolecular H-bond in a series of β -diketones reveals surprisingly long-lived and isotope-dependent orientational dynamics. The orientational dynamics are attributed to activated H atom transfer dynamics driven by internal structural rearrangements. Finally, exciting progress on a novel experimental platform that combines ultrafast IR spectroscopies with cryogenic ion techniques for the acquisition of multidimensional and time-resolved spectra of isolated ion ensembles will be discussed.



Wednesday, October 16, 2024



10:30am



BRWN 4102



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Education

Ph.D., Physical Chemistry, Yale University, 2015. Advisor: Mark A. Johnson.

B.S., Chemistry; Mathematics minor, University of Connecticut, 2010.

Appointments

Assistant Professor of Chemistry, Washington University in St. Louis, 2018-present

Postdoc, University of Chicago, 2015-2018.

Arnold O. Beckman Postdoctoral Fellow, 2016-2018.

Advisor: Andrei Tokmakoff

Awards and Recognitions

At Washington University:

2022 Flygare Award in Molecular Spectroscopy

2021 National Science Foundation CAREER Award

Prior to Washington University:

2016 Arnold O. Beckman Postdoctoral Fellowship.

2015 Richard Wolfgang Prize in Chemistry (best dissertation).

2011-2014 National Defense Science and Engineering Graduate Fellowship.

2011 NSF Graduate Research Fellowship (declined for NDSEG).

One of 24 University Scholars (highest undergraduate distinction at Univ. of Connecticut).

2008 Barry M. Goldwater Scholar.

Publications

At Washington University:

Winkler, V.S.; Fournier, J.A. Characterizing Excited-State Intramolecular Proton Transfer in 3-hydroxyflavone and 3-hydroxy-2-(thiophen-2-yl)chromen-4-one with Ultrafast Transient Infrared Spectroscopy. *ChemRxiv*. **2024**. doi.org/10.26434/chemrxiv-2024-04r7c

Dean, J.L.S.; Cramer, C.G., Fournier, J.A. Interplay between Anion-Receptor and Anion-Solvent Interactions in Halide Receptor Complexes Characterized with Ultrafast Infrared Spectroscopies. *Phys. Chem. Chem. Phys.* **2024**, 26, 21163. doi.org/10.1039/d4cp02280g

Ma, Z.; Chen, L.; Xu, C.; Fournier, J.A. Two-Dimensional Infrared Spectroscopy of Isolated Molecular Ions. *J. Phys. Chem. Lett.* **2023**, 14, 9683. [doi/10.1021/acs.jpclett.3c02661](https://doi.org/10.1021/acs.jpclett.3c02661)

Dean, J.L.S.*; Winkler, V.S.*; Boyer, M.A.; Sibert III, E.L.; Fournier, J.A. Investigating Intramolecular H Atom Transfer Dynamics in β -diketones with Ultrafast Infrared Spectroscopies and Theoretical Modeling. *J. Phys. Chem. A*, **2023**, 127, 9258. [doi/10.1021/acs.jpca.3c05417](https://doi.org/10.1021/acs.jpca.3c05417)

*equal contributions

Chen, L.*; Ma, Z.*; Fournier, J.A. Ultrafast Transient Vibrational Action Spectroscopy of Cryogenically Cooled Ions. *J. Chem. Phys. (Communication)*, **2023**, *159*, 041101. **Editor's Pick article, Cover article.** Included in 2023 Emerging Investigators Special Collection. doi.org/10.1063/5.0155490 *equal contributions

Chen, L.; Sibert III, E.L.; Fournier, J.A. Unraveling the Vibrational Spectral Signatures of a Dislocated H Atom in Model Proton-Coupled Electron Transfer Dyad Systems. *J. Phys. Chem. A* **2023**, *127*, 3362. doi.org/10.1021/acs.jpca.3c00524

Chen, L.; Ma, Z.; Fournier, J.A. Origins of the Diffuse Shared Proton Vibrational Signatures in Proton-Coupled Electron Transfer Model Dyad Complexes. *J. Chem. Phys.* **2022**, *157*, 154308. Editor's Pick article. doi.org/10.1063/5.0122777

Dean, J.L.S.; Fournier, J.A. Vibrational Dynamics of the Intramolecular H-Bond in Acetylacetone Investigated with Transient and 2D IR Spectroscopy. *J. Phys. Chem. B* **2022**, *126*, 3551. doi.org/10.1021/acs.jpcc.2c00793

Chen, L.; Dean, J.L.S.; Fournier, J.A. Time-Domain Vibrational Action Spectroscopy of Cryogenically Cooled, Messenger-Tagged Ions Using Ultrafast IR Pulses. *J. Phys. Chem. A* **2021**, *125*, 10235. Selected for inclusion in the "A Venue for Advances in Experimental and Theoretical Methods in Physical Chemistry" Virtual Issue of JPCA. doi.org/10.1021/acs.jpca.1c01996

Chen, L.; Fournier, J.A. Probing Hydrogen-Bonding Interactions within Phenol-Benzimidazole Proton-Coupled Electron Transfer Model Complexes with Cryogenic Ion Vibrational Spectroscopy. *J. Phys. Chem. A* **2021**, *125*, 9288. doi.org/10.1021/acs.jpca.1c05879

Selected Publications Prior to Washington University:

Fournier, J.A.; Carpenter, W.B.; Lewis, N.H.C.; Tokmakoff, A. Broadband 2D IR Spectroscopy Reveals Dominant Asymmetric H₃O⁺ Proton Hydration Structures in Acid Solutions. *Nat. Chem.* **2018**, *10*, 932. doi.org/10.1038/s41557-018-0091-y

Wolke, C.T.; Fournier, J.A.; Dzigan, L.D.; McCoy, A.B.; Odbadrakh, T.T.; Jordan, K.D.; Fagiani, M.R.; Knorke, H.; Asmis, K.R.; Johnson, M.A. Spectroscopic Snapshots of the Proton Relay Mechanism in Water. *Science*, **2016**, *354*, 1131. doi.org/10.1126/science.aaf8425

Fournier, J.A.; Carpenter, W.; De Marco, L.; Tokmakoff, A. The Interplay of Ion-Water and Water-Water Interactions within the Hydration Shells of Nitrate and Carbonate Directly Probed with 2D IR Spectroscopy. *J. Am. Chem. Soc.*, **2016**, *138*, 9634. doi.org/10.1021/jacs.6b05122

Fournier, J.A.; Wolke, C.T.; Johnson, M.A.; Odbadrakh, T.T.; Jordan, K.D.; Kathmann, S.M.; Xantheas, S.S. Snapshots of Proton Accommodation at a Microscopic Water Surface: Understanding the Vibrational Spectral Signatures of the Charge Defect in Cryogenically Cooled H⁺(H₂O)_{n=2-28} Clusters. *J. Phys. Chem. A*, **2015**, *119*, 9425. (Feature Article, cover art) doi.org/10.1021/acs.jpca.5b04355

Fournier, J.A.; Johnson, C.J.; Wolke, C.T.; Weddle, G.H.; Wolk, A.B.; Johnson, M.A. Vibrational Spectral Signature of the Proton Defect in the Three-Dimensional H⁺(H₂O)₂₁ Cluster. *Science*, **2014**, *344*, 1009. doi.org/10.1126/science.1253788