Columbia University in the City of New York | *New York, NY 10027*

COLUMBIA ASTROPHYSICS LABORATORY

Mail Code 5247
550 West 120th Street

Daniel Wolf Savin
Tel: 212-854-4124
Fax: 212-854-8121
Email: savin@astro.columbia.edu
URL: http://user.astro.columbia.edu/~savin

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Prof. Zdeněk Doležal
Vice Dean of Faculty of Mathematics and Physics
Charles University
Research and International Affairs Department
Ke Karlovu 2027/3, 121 16 Praha 2, Czech Republic

Dear Prof. Doležal:

My report below begins with a general overview of Dr. Roučka's Habilitation and then provides some brief comments on the specific papers included.

Dr. Roučka is one of the leaders in his generation in experimental laboratory astrophysics studies of ion-molecular reactions for astrochemistry. This is clear from his extensive publication record in leading peer-reviewed journals in astrophysics, physics, and chemistry (with 49 publications, over 1235 citations, and an h-index of 11). Of the nine publications that form the core of his Habilitation, seven have already been published and two have been submitted for publication. As an aside, I note that the high Turnitin score is due to the fact that Dr. Roučka's Habilitation is, in part, a collection of reprints of these seven published papers co-authored by him and does not indicate any scientific misconduct regarding plagiarism.

Dr. Roučka has studied a range of chemical reactions, some of which are important for astrochemistry and some of which are of fundamental interest for physical chemistry (also sometimes referred to as chemical physics or molecular physics). My expertise is in experimental laboratory astrophysics studies of ion-molecular reactions for astrochemistry, and so my review will focus mostly on that aspect of Dr. Roučka's Habilitation.

It is clear from the introductions in Dr. Roučka's publications that his experimental laboratory astrophysics studies are extremely well motivated by observational and modeling studies in astrochemistry. His citation of the published literature demonstrates a deep knowledge of the state of the field of molecular astrophysics and of what laboratory measurements are needed to move the field forward. It is also important to mention that molecular theory is unable to reliably provide much of the astrochemical kinetics data needed to interpret astronomical observations of molecular sources. Fully quantum mechanical reactive scattering calculations are at the forefront of being computationally possible for three-atom systems and just beyond for four-or-more-atom systems. Semi-classical methods using classical trajectories on quantum mechanical potential energy surfaces and fully classical methods, such as the Langevin approach, can have large uncertainties. Laboratory measurements, such as those being performed by Dr.

Roučka, are the only way to provide reliable kinetics data for astrochemical models and observations. My one recommendation for Dr. Roučka is that in future works he should bring his laboratory astrophysics measurements full circle and explore the astrochemical implications of his findings. One way to do this might be to download one of the publicly available astrochemical models, modify it with his groups new rate coefficients, and explore the changes in predicted molecular abundances.

Here now are some brief comments on the papers included in Dr. Roučka's Habilitation.

Paper A: D^- + H Associative Detachment. This is an isotopic study of one of the most fundamental anion-neutral chemical processes. It also happens to be nicely complementary to the H^- + H and D^- + D associative detachment measurements that my group carried out. Experimental studies such as these are needed to benchmark theoretical methods for two-atom reactive scattering systems. The good agreement between theory and experiment enables the theorists to more reliably extend their methodology to three-or-more-atom systems.

Paper B: Formation and Internal Structure of D_3O^-. Ternary rate coefficients are important for gas-phase atmospheric, laboratory, and industrical chemistry. This paper on the role of ternary processes in the formation of negative cluster ions provides an important set of laboratory benchmarks for understanding the cluster formation process and for future theoretical developments in this area.

Paper C: Rotational Excitation of H_2 in Reaction with OD^-. Ortho- and para-H_2 essentially function as two separate chemical species in astrochemical environment and it is important to understand how their differing quantum states affect various scattering processes. This study provided needed kinetics data for modeling OD^- in molecular clouds.

Paper D: Formation of H_2O^+ and H_3O^+. These two ions are important for the gas-phase formation of H_2O in the interstellar medium (ISM). Tracing the formation of water in the ISM is important for astrobiology. The importance of this work is demonstrated, not only in this publication, but also by the fact that a later study by a different group was published in Science Advances (Kumar et al. 2018, Sci. Adv, 4, eaar3417). That group's work showed excellent agreement with Dr. Roučka's results.

Paper E: OH^+ Formation in the $O^+(^4S)$ + H_2 Reaction. This is another important reaction in the gas-phase chain of chemical reactions leading to the ISM formation of water. In combination with the work in Paper D, these results improve the model predictions for the gas-phase formation of water. Remaining discrepancies between the gas-phase model and observations can be used to tell us about the physical properties of the molecular sources and not about our lack of understanding of the underlying astrochemistry.

Paper F: Reaction of NH^+, NH_2^+, and NH_3^+ Ions with H_2. Ammonia is an important molecule in the chemical pathway from atoms in space to life as we know it. For this reason, understanding the formation of ammonia in the ISM is an active area of research. This work provides important kinetics data for observations and gas-phase formation models of ammonia in the ISM.

Paper G: The Reaction of $O^+(^4S)$ Ions with H_2, HD, and D_2. This is a continuation of the study reported in Paper E, extending the work to isotopologues of H_2. The primary focus of this work is on fundamental chemistry. But deuterated chemistry is also important in cold molecular clouds, where the low temperatures result in an enrichment of HD and D2 by several orders of magnitude above that expected considering the Galactic D-to-H ratio of about 10^{-5}. This enhancement is because the vibrational zero-point energy of the deuterated isotopologues is lower than that of H_2. At sufficiently low temperatures, the exoergic deuterating reactions

will go forward, but the reverse endoergic hydrogenating reactions cannot proceed, leading to an enhancement in the D-bearing isotopologues, which provide valuable astrochemical diagnostics for these environments.

Paper H: Reaction of N^+ with H_2, HD, and D_2. This unpublished manuscript reports one of the initial steps in the gas-phase formation of ammonia in the ISM. It is important for the reasons given above for Paper F and the deuterated reactions for the reasons given above for Paper G.

Paper I: Endothermicity of the N^+ + H_2 Reaction. This unpublished manuscript is a study in fundamental chemistry, but provides information that will be needed for astrochemical models for the reasons given above for Papers F, G, and H.

In summary, Dr. Roučka's Habilitation Dissertation represents an impressive body of work and I strongly support his being awarded the Hablitation.

Sincerely,

Daniel Wolf Savin, Ph.D.
Senior Research Scientist, Columbia Astrophysics Laboratory
Senator, Columbia University (CU) Senate
Chair, Research Officers Committee, CU Senate
Co-Chair, Structure and Operations Committee, CU Senate
Member, Budget Review Committee, CU Senate
Fellow, American Astronomical Society
Science Editor, Journals of the American Astronomical Society
Fellow, American Physical Society