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Review of the Habilitation Thesis
» Astrophysically Relevant Reactions of Ions with Molecular and Atomic Hydrogen «
by
Dr. Štěpán Roučka

Dr. Roučka presents in his Habilitation Thesis a series of seven published scientific papers, a commentary, and the manuscripts of two further scientific articles whose publication is under way. The commentary describes the guiding ideas of the research work and the connections between the results as contained in the publications.

The covered scientific work represents an important area of physical research in which laboratory plasma under a very high degree of external control is used to mimic conditions that occur in low-density, ionized regions of the interstellar space and also in planetary atmospheres, including the outer zones of the terrestrial atmosphere. The laboratory instruments are highly sophisticated, requiring years-long development that Dr. Roučka has obviously been strongly involved in, and based on the trapping of ions in external electromagnetic fields. Research on ion trapping is a front-line area of experimental physics with relevance from fundamental particle physics and quantum physics to the investigation of chemical reaction dynamics and the study of complex macro-molecular matter. In Dr. Roučka's studies, small samples of trapped ions are prepared by cryogenic cooling in an inert buffer gas. The ion trap then mixes the cooled ions with a low-density gas of neutral molecules in an isolated reaction volume, where well-defined binary reactions between the stored ions and a neutral reacting molecule can be studied. Over storage times up to many seconds, product ions are formed and possibly further react within in the storage volume, until the electromagnetic trap is opend and the ion inventory is analyzed, identifying the amount of ions with different molecular masses then present. By repeating many experiments for constant storage conditions and initial states, the amount of the initial and of any product ions can be tracked as a function of time spent in the cryogenic reaction volume, and reaction rates can be determined. As realized in this work, this method is very direct and powerful for studying ionic reactions under extreme, externally controlled conditions.

As a basis for the research documented by his Habilitation Thesis, Dr. Roučka has ensured the perfect control of the ion trapping technology from the laboratory hardware to the data analysis; he shortly summarizes some related aspects in the introduction to his comment chapters. His presented works have also extended the range of neutral reaction partners by operating next to the ion trap a diffusive-beam source for atomic hydrogen, including cryogenic accomodation of the hydrogen atoms. Moreover, control of the nuclear spin states of molecular hydrogen was implemented, becoming important for the chemical reactivity at cryogenic temperatures. Both latter aspects underline the complexity of the laboratory technology connected with Dr. Roučka's research.

The two main, new areas addressed in the presented publications are reactions with hydrogen atoms and hydrogen molecules at cryogenic temperatures (a) with light and important negative ions (especially the atomic hydrogen anion H^- and the hydroxyl anion OH^- and its deuterated forms) and (b) in the low-temperature range for a wide range of hydrogenated oxygen and nitrogen ions (OH_n^+, $n = 0 \ldots 2$ and NH_n^+, $n = 0 \ldots 3$). The studied ions are considered in astrophysical models by an international research community. While the positive hydrogenated ions play a particular role in the formation of water and ammonia in interstellar ion chemistry and are not only modeled, but partly also spectroscopically observed, the studied anions are of interest in the modeled chemical reaction chains (including the cosmological evolution, as regards H^-), although observationally, searches for them are ongoing. The effects of deuteration and of the nuclear-spin properties of molecular hydrogen, also studied in the presented work, are as well important in the astrophysical models.

Taking the seven published articles (referred to by A-G in the Habilitation Thesis), each of the papers not only presents reaction-rate data on an absolute scale, as valuable for the astrophysical models, but also carefully, as far as possible, adresses the underlying quantum physics of the reactions and the depencence of their rates on the quantum states of the reacting partners. In paper A on D^- + H, cross sections for the dissociative electron detachment to form HD are derived both experimentally and theoretically. Moreover, also the resonant electron transfer process yielding H^- + D products is measured and calculated. Paper C on OD^- + H_2 studies the influence of the H_2 rotational excitation on the reaction rate. Paper D on oxygen reactions is unique in systematically studying the temperature dependences of the H_2 reaction rates for both OH_n^+ ($n > 0$) product reactions in the water production chain, while paper E addresses the initial step ($n = 0$) in the water-formation chain, $O^+ + H_2$, and results in reliable data for the temperature dependence of the reaction rate suppressing possible fine structure excitation of the O^+ ions. Paper F in a comparable way to paper D yields the so far unknown temperature dependences of the H_2 reaction rates for molecular NH_n^+ reactions ($n > 0$) in the ammonia production chain. The recent publication G extends the studies on the O^+ reaction in paper E to the deuterated variants of H_2, also ensuring that the results are valid for the fine-structure ground state of the O^+ ions. The results of papers G and E together show a similarity of the cross sections for the reactions with H_2 and HD and an about 30% smaller reaction rate for D_2. Moreover, the branching ratio of OH^+ and OD^+ products in the HD reaction is found to be close to 50%. Here, a microscopic interpretation of the results is not given, especially considering that the relative rates for the three isotopic variants deviate from those from a simple rate model (Langevin model). However, the given absolute isotopically dependent rate coefficients will still be highly useful for astrophysical models considering reactions of deuterated molecules.

These published articles A-G represent a new data set on the oxygen and nitrogen ion chemistry in the interstellar medium, making use of the improved ion trapping method. The low-temperature range for the reaction rates is systematically made available, so that the data directly fit the data need of astrochemical models, including ongoing efforts to understand the molecular effects on deuteration in the interstellar medium. The publications are well documented and the integrity of the data is ensured by careful and critical analysis. The works have been published in the central and highest-level international scientific journals of the research field. The set of publications clearly underlines the Dr. Roučka's excellent qualification for planning and realizing scientific research of broad interest in this experimentally challenging field of knowledge.

Dr. Roučka also presents two so far unpublished manuscripts (papers H and I) concerning measurements on the collision processes $N^+ + (H_2, HD, \text{and } D_2)$ and on the pair of mutually reverse reactions, $N^+ + H_2$ and $NH^+ + H$, also based on ion trapping measurements. He complements these manuscripts by discussions in section 3.3 of the comments in his Habilitation Thesis. Both topics address in particular the extraction of molecular energetics (the isotope-independent electronic energy difference and the reaction endothermicity for the $N^+ + H_2$ reaction) from reaction rate measurements. These so far unpublished works are of interest for chemical physics because of the intrinsic molecular properties derived, where in particular data on molecular binding energies derived in paper I are still lacking for many elementary molecules. While not yet finally published, and ambitious regarding the interpretation of the measured reaction rates, these works usefully complement the Habilitation Thesis and also illustrate attractive future developments of the research.

Altogether, already the collection of publications A-G, together with the comments in the thesis on the context of the different measurement and on the newly implemented properties of the experimental setup, document the impressive scientific quality of the research work presented in Dr. Roučka's Habilitation Thesis. The further added manuscripts H and I, together with the comments, as a supplement point towards promising future achievements of the scientific work opened up by Dr. Roučka's activities. The presentation of the work in the thesis is highly convincing, and documents attractive applications of the achieved results.

The comment part of the thesis is, such as also the publications are, well written and carefully presented. I took note of the markings from the plagiarism-check system concerning this part. The highlighting by the system is limited to short text fragments rarely exceeding one line. All regard commonly used scientific language of the field. The only few-line-long passages I saw, indicate that captions of figures reproduced in the comment did not differ strongly from those in the original publications (such as figure 3 of the comments and paper A). This, however, is completely in agreement with the idea of the comment and is, moreover, made transparent by suitable citation. So, none of the markings in any way compromise the originality of the work.

In summary, the Habilitation Thesis shows that Dr. Roučka made highly valuable contributions to the understanding of elementary reactions of ion chemistry at low temperature and also demonstrates attractive future perspectives of the research. The Habilitation Thesis is of excellent scientific excellent quality.

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