Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA21126

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Details of the STSM

Title: Astrochemistry of third raw elements: unraveling the ionic reaction pathways leading to Si and P containing species

Start and end date: 02/07/2024 to 08/07/2024

Description of the work carried out during the STSM

The research topic addressed in this STSM concerns gas-phase ion-molecule chemistry, which could lead to Si- and P-containing ionic or neutral species, such as SiO, SiC, SiN, SiS, SiP, SiC_2, SiCN, PO/PO^+, PN, CP, C_2P HCP, PH_3, etc. that have already been detected or are expected to be present in various astronomical environments. The aim of the STSM was to participate in experiments planned at the DESIRS VUV beamline of the French National Synchrotron Facility SOLEIL to generate from suitable precursors Si^+ and P^+ reactant ions and collect data on the reaction with a range of astrochemically relevant neutral molecules, with a particular focus on reactions leading to the build-up of chemical complexity.

Experiments performed during the STSM

Experiments have been performed using the CERISES set-up associated with the DESIRS beamline. CERISES is a guided ion beam tandem mass spectrometer in which the ions are generated by tuneable VUV light, selected by quadrupole mass filter and guided using RF octupole into the collision/reaction cell. The products of ion-molecule reactions taking place in the collision/reaction cell are analyzed by the second quadrupole mass filter and detected by electron multiplier. The data from this experimental setup provide absolute integral cross sections and product branching ratios for ion-molecule reactions as a function of collision energy (in the range from meV to tens of eVs).

The precursor ions $Si^+(^2P)$ and $P^+(^3P)$ were generated by dissociative photoionization of $SiCl_4$ and PCl_3 in the range of 22-30 eV and 13-30 eV, respectively. The observed appearance energy for $Si^+(^2P)$ was ~23 eV, with a maximum yield at ~27.5 eV. For PCl_3, the appearance energy of $P^+(^3P)$ was observed at ~15.5 eV (corresponding to the opening of the fragmentation channel $P^+(^3P)+Cl+Cl_2^-$), but the ion yield curve shows a second more intense appearance threshold at ~20.5 eV (corresponding to fragmentation into $P^+(^3P)+3Cl$) before reaching its maximum yield at about 23.6 eV photon energy. Additionally, at a photon energy ~23.1 eV (i.e. ~2.6 eV higher than the second threshold), the production of P^+ in its second

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

metastable excited state (^1S) was indirectly observed. Reactions of Si^+ with H_2S, D_2, CH_3NH_2, CH_3CN, CD_3CN, NH_3, CH_3CH_2CN, CD_3CD_2CN and CH_2CHCN were studied, and reaction data for the laboratory-frame collision energies (E_{lab}) in the range 0-20 eV were collected. Similarly, the P^+ ion reactivity with H_2, D_2, N_2, O_2, C_2H_2, C_2H_6, CH_3CN, CD_3CN, CH_3CCH, H_2CCCH_2 and CH_2CHCN was studies in the same E_{lab} range.

In addition to all these experiments, CO_2 was used to generate CO^+ and C^+ reactant ions. The former ion, isobaric with Si^+, was used to check the reactivity with CH_2CHCN to exclude or to correct for possible contamination of the Si^+ ion beam due to leaking air into the ion source region of the CERISES. The reactivity data of the latter ion with CD_3CN was acquired to complement data from the previous beam time, in which the reactivity of C^+ with CH_3CN was studied. As the CERISES apparatus has only unit mass resolution, using isotopically labeled reactants is sometimes necessary to determine unambiguously the elemental compositions of ionic products.

Description of the STSM main achievements and planned follow-up activities

The STSM successfully managed to achieve all of its planned goals as listed in the grant application. However, certain modifications had to be made as indicated and justified below.

1) The reaction of $Si^+ + H_2S$ was studied and SiS^+ and $SiSH^+$ product ions were observed. The reactivity of Si^+ with H_2O was not studied for practical reasons (the “stickiness” and resulting memory effect of the H_2O on the inner walls of the apparatus).

2) Reactions of Si^+ with small hydrocarbons and nitriles were studied. The list of the neutral reactants involved in these experiments was modified (*vide supra*) with respect to their availability and stability. Originally planned HCN, HC4H and HC3N would have to be synthesized on site, and moreover, HC4H is very unstable. Several interesting species, $SiCH_2^+$, $SiCNH^+$, $SiC_2H_4^+$ and $SiCH_2CN^+$, to name a few, were observed in these experiments. Reactions with SiH^+ were not studied due to the unavailability and hazardousness of the SiH_4 precursor. Moreover, it would also require a change of the beamline grating.

3) The reactions $P^+ + H_2/D_2 \rightarrow PH^+/PD^+ + H/D$ were studied as planned. The experimental results at high collision energies will serve as a benchmark for the high-level ab initio calculations to be performed by Alexandre Zanchet and his colleagues.

4) The reactivity of P^+ with H_2O was not studied for the reasons mentioned above. Instead, the data for reactions with several other reactants (*vide supra*) were recorded. The choice of neutral targets was dictated by the fact that for most systems no experimental or theoretical data on their kinetics were available. Among very interesting and important products, ionic species such as PCH^+, PCH_2^+, $PC_2H_2^+$, $PC_2H_4^+$ and PNH^+ were detected, and the formation of neutral PN and PCN molecules was inferred from the experimental data. Rather surprising was also the formation of PN^+ ions upon the reaction of P^+ with N_2 at higher collision energies ($E_{coll} > 5$ eV).

All the experimental data acquired during this STSM are currently being processed and analyzed, and the complete set of photon energy and collision energy-dependent cross sections and branching ratios will serve as a basis for preparing several manuscripts.

The experimental data will be complemented by high-level *ab initio* calculations. In particular, the STSM’s grantee will perform calculations aimed at mapping the potential energy surface representing reactions of $Si^+(^2P)$ with nitriles (CH_3CN, CH_2CHCN and CH_3CH_2CN) to discover details of the possible structures of reaction products, corresponding reaction mechanisms and energetics.

The results obtained during this STSM, i.e., the ion-molecule reaction collision cross sections and branching ratios, are expected to be relevant to shaping the knowledge of the chemistry of Si- and P-containing carbonaceous molecular species in space and to contribute to the Action objectives.