

Dynamics of ion-molecule reactions of SO_2^+ with H_2O and CH_4

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Synopsis. The reaction dynamics and the temperature-dependent kinetic trend of the SO_2^+ ion-molecule reactions with water and methane have been studied using the tunable synchrotron radiation to produce excited SO_2^+ ions and ab-initio methods. The experimental results show that only one product, HSO_2^+ , is formed in both reactions and its yield displays different trends with the photon energy. DFT and VTST calculations have been used to explore the dynamics of the reactions and to calculate the rate constants at different temperatures.

The different reactivity of O-H and C-H bonds in the reaction of water and methane with SO_2^+ is of fundamental interest due the dynamical processes occurring along the reaction paths on the potential energy surfaces. Moreover these reactions in the gas phase are considered as a laboratory model of the chemistry of terrestrial and planetary atmosphere as well as of the molecular synthesis in the interstellar space. [1] The experiments have been performed at the “Circular Polarization” beamline (CiPo) of ELETTRA (Trieste, Italy) [2] where monochromatic VUV photons of tunable energy (12-14 eV) were used to ionize the SO_2 molecules from an effusive beam. In this energy range considering the lifetime of the SO_2^+ ionic excited states ($^2\text{B}_2$ and $^2\text{A}_2$), the ion can be considered to be in excited rovibrational levels of its ionic ground state X^2A_1 before reacting with the neutrals. In Figure 1 the ratio $\text{HSO}_2^+/\text{SO}_2^+$ for the two reactions is reported versus photon energy (i.e. increasing internal energy of the SO_2^+ ion). The trend for the two reacting systems is different: the reaction is decelerated in the water case, while it is firstly decelerated and then accelerated in the case of methane. Theoretical calculations allowed to obtain the minimum energy paths (MEPs) for the two reactions and to localize the variational transition state VST, the bottleneck of the reaction, to calculate the rate constants k of the two reactions. The trend of k in the range of 298-500 K (12.4-12.8 eV) reproduces quite well the experimental data [5] and the dynamics of the two reactions explain in exhaustive way the higher reaction efficiency ($\phi=k/k_{\text{coll}}$) with water than with methane measured and reported in previous works at 298.15 K [3,4]. Further experimental work has been undertaken to investigate the SO_2^+ reactions with H_2/D_2 , which are relevant for astrochemistry.

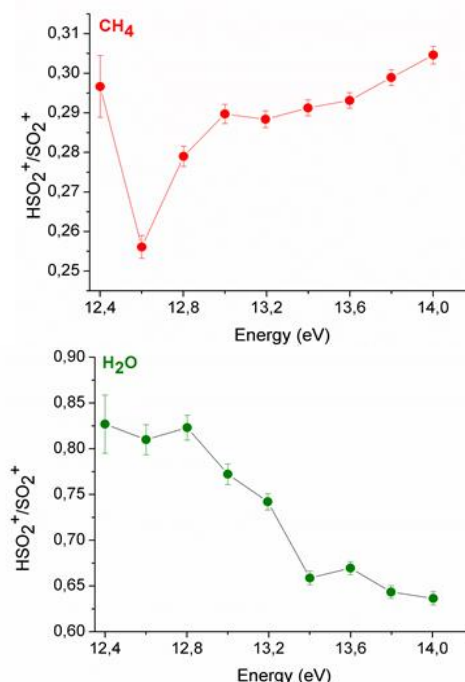


Figure 1. $\text{HSO}_2^+/\text{SO}_2^+$ ratio vs photon energy in the reaction of SO_2^+ with methane (top) and water (bottom), at the fixed pressure of 1.0×10^{-5} mbar and nominal collision energy of 0 eV.

References

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