HSO_2^+ formation from ion-molecule reactions of $SO_2^{\cdot+}$ with water and methane: two fast reactions with reverse temperature-dependent kinetic trend

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Abstract: In this work an experimental and theoretical study on the formation of HSO_2^+ ion from the $SO_2^{\cdot+}$-CH_4 and $SO_2^{\cdot+}$-H_2O ion-molecule reactions at different temperatures is reported. Tunable synchrotron radiation has been used to produce the $SO_2^{\cdot+}$ ion in excited vibrational levels of the ground state and mass spectrometry has been employed to identify the product ions. Calculations in the framework of the density functional theroy and variational transtition state theory have been combined to explore the potential energy surface of the reactions. The experimental results show that the only product in both reactions is HSO_2^+. Its yield decreases monotonically with photon energy in the $SO_2^{\cdot+}$-H_2O reaction, while it decreases at first and then increases in the $SO_2^{\cdot+}$-CH_4 reaction. Theory confirms this trend by calculating the rate constants at different temperatures and explains the results by means of the polar, spin and charge effects as well as structural reorganization occuring in the reaction coordinate. This study provides new insights on the reactivity of sulfur dioxide ions relevant for astrochemistry and the chemistry of activation of simple molecules.

Introduction

The study of ionic processes in the gas phase has a fundamental and applicative relevance in several fields of chemistry and physics such as astro and atmospheric chemistry,[1] biophysics,[2] activation and/or functionalization of simple starting materials.[3] The interest spans from the study of the photofragmentation of ions and charged clusters to the formation of charged species, molecules and radicals from chemical reactions. Thus much effort has been devoted to study ion-molecule reactions in the gas phase, considered as a model laboratory of the chemistry of terrestrial and planetary atmosphere, and of the molecular synthesis in the interstellar space.[4] Moreover, some of these reactions have also been identified to be suitable models for more complex processes. Hence a coherent and complete investigation of the kinetic, thermochemical and mechanism features of these reactions has to be considered of paramount multidisciplinary interest.[5] The efficiency and reaction rate of the ion processes are usually obtained at thermal condition and room temperature. However, excited ions at higher temperature are often involved in many processes, for instance in space, where energetic electrons, photons and particles can ionize molecules. The purpose of this work is to investigate this unexplored regime in the formation of the ionic species HSO_2^+ from the SO_2 molecule. Sulfur dioxide, one of the main sulphur-containing molecules, is present on Earth and it has been observed in the interstellar space for the first time in 1975[6] and successively in molecular clouds, hot corinos together with sulphur-containing positive ions, like SH^+.[7] SO_2 is also present in extraterrestrial atmospheres, and it is the main constituent of Jupiter's satellites Io. Furthermore its ion $SO_2^{\cdot+}$, probably generated from ionization of SO_2 by Jupiter's plasma, has been detected by Galileo spacecraft.[1a] It appears that, despite the presence of these neutral and ionic species in several astrophysical environments, there is an unexpected lack in both experimental and computational study of its reactivity. In its neutral (SO_2) and cationic charge state ($SO_2^{\cdot+}$) the simplest, most fundamental and widespread reactions with a general compound R-H involve the proton transfer, (PT, H^+), from R-$H^{0/+}$ to SO_2 and the hydrogen atom transfer, (HAT, H), from R-H to $SO_2^{\cdot+}$ both leading to the same ionic product, HSO_2^+.[8] Despite the protonated sulphur dioxide has not yet been detected in space, the growing field of the interstellar ion-chemistry and the rotational spectra data collected in laboratory[9] will certainly help identifying this ion. Hence reactions that produce HSO_2^+ and the kinetic trend of the reaction with the temperature are relevant to understand the reactive network of sulfur-containing compounds. In this work the study of the formation of HSO_2^+ at different temperatures and internal energies from the ion-molecule reaction between the excited ion $SO_2^{\cdot+}$ and methane and water compounds is reported. The choice of these molecules is due to their presence in various environments in space [10] but also to their fundamental importance in model studies of bond activation and functionalization of organic compounds. Actually the reactions involving the O-H and C-H activation have been the object of many studies and the mechanistic aspects are still under debate.[11] As reported in the literature and confirmed in the

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present work the HAT reactions are faster in the O-H case, despite the higher or similar binding energy of O-H with respect to C-H in several molecules.[12] In the case of water (O-H Bond Dissociation Energy, BDE=497.1 kJ mol^{-1}) and methane (C-H, BDE= 439.3 kJ mol^{-1}) the difference is 57.8 kJ mol^{-1}.[13] The different reactivity of O-H and C-H bonds in the reaction with $SO_2^{\cdot+}$ has an interest connected with the dynamical processes occurring along the reaction paths on the potential energy surfaces. In this work the variational transition state theory (VTST)[14] has been used to obtain the rate constants of the two reactions as a function of the temperature and the trend is compared with the experimental results obtained with tunable synchrotron radiation. Moreover the theory has allowed to elucidate the mechanistic aspects and to explain why $SO_2^{\cdot+}$ reaction with water is faster and more efficient than the one with methane. This joint experimental and theoretical study will provide new kinetic and mechanistic insights on the reactivity of the sulfur dioxide ions relevant for astrochemistry as well as for chemistry of activation and functionalization of simple model molecules.[15] All along the test the point $^{\cdot}$ in $SO_2^{\cdot+}$ has been omitted for the sake of simplicity.

Results and Discussion

The experiments were performed at the "Circular Polarization" beamline (CiPo) of ELETTRA (Trieste, Italy) [16] where monochromatic VUV photons of tunable energy were used to ionize the SO_2 molecules of an effusive beam. The apparatus for ion-molecule reaction studies (Figure 1S in SI) consists of an octupole ion-guide and a quadrupole mass spectrometer. The SO_2^+ ions are transported into the octupole by an extraction optics, which also defines their collision energy, CE. The neutral reacting molecules are introduced in the octupole at a controlled pressure and the charged products are analyzed by the quadrupole mass spectrometer. The ion-molecule reaction measurements were performed recording the ion yields of ionic reagent and products as a function of the photon energy, hν, at fixed collision energy and pressure. Details of the set-up and procedures are collected in the Experimental section. In order to interpret the results, the structure of the energy levels and photofragmentation of SO_2 in the VUV range have to be considered. The photoelectron spectra of SO_2 in the energy range 12-14 eV are characterized by two bands.[17] The first band (12-13 eV) corresponds to the ionic ground X $^2A_1$ state (12.349 eV) while the second band (13-14 eV) is assigned to the two excited electronic states $^2B_2$ and $^2A_2$[17c] which are very close in energy, their binding energies being 12.988 and 13.338 eV respectively. Photoelectron-photoion coincidences (PEPICO) experiments demonstrated that in these electronic states the parent ion SO_2^+ is stable and it doesn't dissociate.[18] Indeed the appearance energy (AE) of the first fragment ion SO^+ (m/z 48) (AE) is about 16.0 eV[19] as confirmed in this work where AE(SO^+)= 16.05±0.05 eV has been measured (Figure 2S, see SI). At the photon energy lower than 13.0 eV the SO_2^+ parent ion can be formed in the fundamental or vibrationally excited ground electronic state $^2A_1$ (first band, IP= 12.349 eV). When the photon energy is close to 13.00 eV, but lower that 13.338 eV, the first excited state $^2B_2$ of SO_2^+ is also produced. However, the conical intersection (CI) between 1^2A_1 and 1^2B_2 , makes $^2B_2$ convert into $^1A_2$ in a femtoseconds time scale. [20] Moreover, the excitations to higher ion electronic states as the $^2A_2$ one (IP=13.338 eV) are characterized by decays to the ground ionic state with lifetimes shorter than 10 ns.[21] All the above processes occur on a time scale shorter than the travelling time of SO_2^+ from the ion source to the reaction zone (octupole), which has been estimated to be of a fraction of μs. Hence, the SO_2^+ ions produced under vacuum condition of about 10^{-6} mbar and at hν > 12.349 eV can be considered to be in excited vibrational levels of the ionic ground state, which are those actually involved in the reactions. Taking into account the above considerations, in the following only the ion ground state dynamics has been considered. The ion-molecule reactions of these "hot" SO_2^+ (m/z 64) with both water and methane give the product ion HSO_2^+ (m/z 65) as clearly shown in Figure 1.

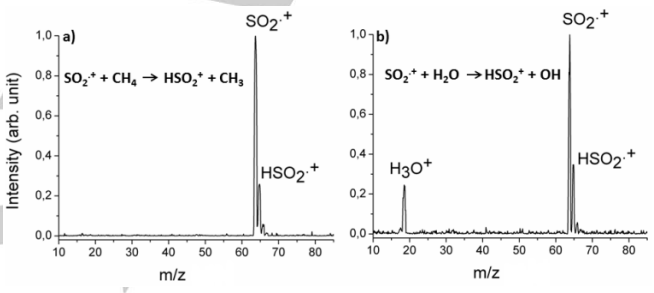


Figure 1. Mass spectra (m/z in amu) recorded at the photon energy of 14.0 eV, Collision Energy (CE) =0 eV and $P_{H2O/CH4}$=1.0x10^{-5} mbar for the reactions of $SO_2^{\cdot+}$ with a) CH_4 and b) H_2O.

In the water case the ion at m/z 19 (H_3O^+) is also observed as the further reaction of HSO_2^+ with another water molecule.[4a] The yields of both HSO_2^+ and SO_2^+ ions have been measured in the two reactions, at CE=0 eV and fixed pressure of the neutral reagent. Their ratios (HSO_2^+/SO_2^+) have been plotted as function of photon energy in Figure 2.

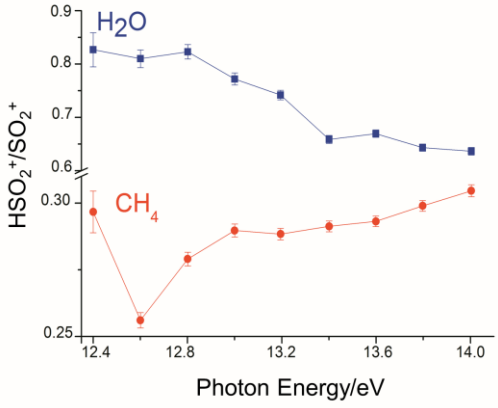


Figure 2. HSO_2^+/SO_2^+ ratio vs photon energy measured for the reaction of SO_2^+ with water (blue) and methane (red), at the fixed pressure of $1.0x10^{-5}$ mbar and CE=0 eV. The pressure of the reagent gas SO_2 in the ion source is $6.2x10^{-6}$ mbar.

The results for photon energy in the 12.0-14.0 eV range, show that in the reaction with methane the HSO_2^+/SO_2^+ratio decreases at first (until 12.6 eV) and then increases, while it monotonically decreases in the water case. The same trend is observed in other experimental conditions where i-the collision energy (CE=0.5 and 1.0 eV, Figure S3 in SI) is changed; ii-the pressure of the neutral reagent is varied and iii- the intensity of the ion at m/z= 19 is included in the calculation of the ratio in reaction with water $((HSO_2^+ + H_3O^+)/SO_2^+$, Figure S4 in the SI). The different trends of the ratios with photon energy, namely internal energy of ion, is quite intriguing since both the reactions lead to the same product ion HSO_2^+ through a HAT from CH_4/H_2O to SO_2^+. It is known that at the thermal condition of 298 K, SO_2^+ reacts with water and methane with a rate constant $k= 2.60x10^{-9}$ and $6.58x10^{-10}$ ± 30 % $cm^3s^{-1}molecule^{-1}$ respectively and the collision efficiency, ϕ, relative to the collision rate[22] of the reaction is higher with water than methane, being 100% and 64 % respectively.[11e,f] In this study new aspects have been investigated. The first aim of the work was to explain the different efficiencies of the two reactions, and the second one, more challenging, to explore how the internal energy of the SO_2^+ in its ionic ground state affects the reaction with water and methane.

In the experiment with synchrotron radiation and in collisionless conditions, the internal energy of the SO_2^+ ion in its ground electronic state, increases when the energy used to ionize the SO_2 molecule is higher than 12.349 eV. The excited SO_2^+ ions result in different reactivity with methane and water as shown in Figure 2. In order to understand these relevant aspects an extensive theoretical study has been performed. DFT and VTST calculations have been combined to explore the potential energy surface (PES) of the reactions and to provide insights into the factors controlling the reaction rates. For both reactions the lowest energy path which controls the hydrogen migration to SO_2^+ is associated with the cis conformation of the reaction complex, where the methane or water molecule bounds to one of the O atoms of SO_2^+ via the lone pair orbital in cis conformation with respect to the other O-atom.

In Figure 3 the minimum energy paths (MEP) of the two reactions are shown. Using the VTST approach,[23] for both reagents CH_4 and H_2O, we searched along the MEP, the geometry of the reaction complex at which the reaction flow is at its minimum: this geometry corresponds to the variational transition state configuration (VTS, indicated with red rhombus in Figure 3.) which is the "bottleneck" of the reaction, namely where the evolution of the reaction is slowest. It is worth noting that for reactions having an energy barrier between reagents and products, the activated complex geometry, namely TS, is the molecular configuration corresponding to the highest energy point of the barrier. Instead, barrierless exothermic reactions have the TS localized at some point along the MEP in between reagents and products. Moreover when the reactions are extremely fast the VTST predicts that the TS is localized in the region of the MEP close to the products (for details see Theoretical section and Table S1 in SI).

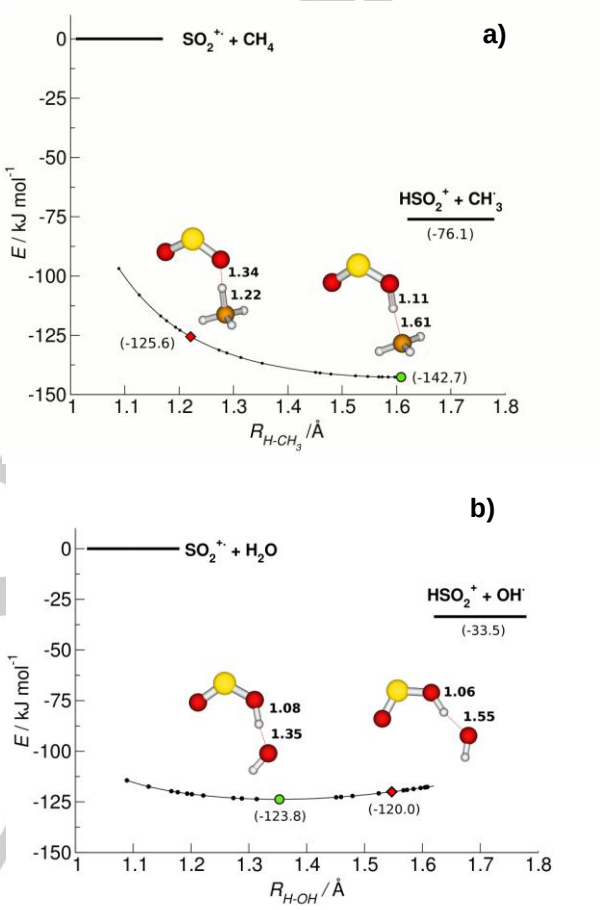


Figure 3. PES of the hydrogen transfer reactions between $SO_2^{+\cdot}$ and a) methane and b) water. The structures, computed at the B3LYP/6-31++g** level of the theory, represent the VTS (rhombus, red) and the minimum (circle, green) energy geometries. Charges are omitted for the sake of clarity.

As it can be seen in Figure 3, both reactions are barrierless and exothermic for 76.1 kJ mol^{-1} (CH_4) and 33.5 kJ mol^{-1} (H_2O) and lead to HSO_2^+ and CH_3/OH radicals. The main difference observed along the reaction coordinate, is the location of the VTS. In the reaction with methane, VTS (Figure 3a, -125.6 kJ mol^{-1} in) is close to the reagents (early TS) and before the minimum (MIN) (green circle, -142.7 kJ mol^{-1}) structure, which is close to the products. Instead VTS is close to the products (late TS, Figure 3b, at -120.0 kJ mol^{-1}) and after the MIN (-123.8 kJ mol^{-1}) in the reaction with water. In both systems the geometries at the minima reflect those of their respective final products, with CH_3 and OH radical bond to the HSO_2^+ ions. Only in the reaction with methane the VTS, being near the reagents, has a geometry

far from that of the products and the two moieties, SO_2 and CH_4, maintain their identity with the H atom mainly belonging to methane (bond length of C-H 1.22 Å against 1.34 Å of O-H in HSO_2, see Figure 3a). On the contrary, in the water case the MIN and VTS are both late and close to each other in the reaction coordinate and hence have similar geometry: the O-H bond length in HSO_2 is 1.08 Å in MIN and 1.06 Å in VTS (see Figure 3b). Therefore, the VTS in SO_2^{+}-H_2O reaction, being in the region of the products where hydrogen atom transfer has been almost completed, does not hamper the reaction, which is fast and complete. This simple picture, proposed for the first time with the VTST, already justifies and allows shaping up the collision efficiency, ϕ, to 100% for the reaction of $SO_2^{\cdot+}$ with H_2O.

To explore possible factors that make reaction faster with water than with methane, the electronic distribution of the molecules have also been considered and the distributions of the charge and spin of the two systems has been investigated (Figure 4 and 5). Interestingly, the faster reaction with water reflects the evidence that the difference in BDE of 57.8 kJ mol^{-1}[13a] of O-H in water relative to C-H in methane, is not the only factor determining the rate constant.[12a,b],[24]

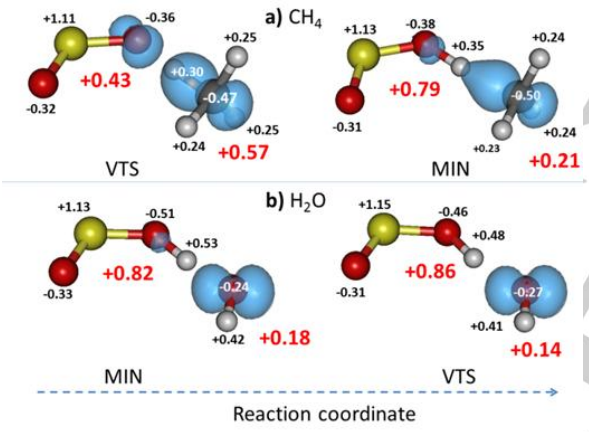


Figure 4. Charge (in e) and spin distribution (blue isosurface) at the B3LYP/6-31++g** level of the theory in the atoms of VTS and MIN optimized structures obtained for the reaction of SO_2^{+} with a) methane and b) water. The numbers in red are the total charge in SO_2, HSO_2, CH_4, CH_3 and OH moieties.

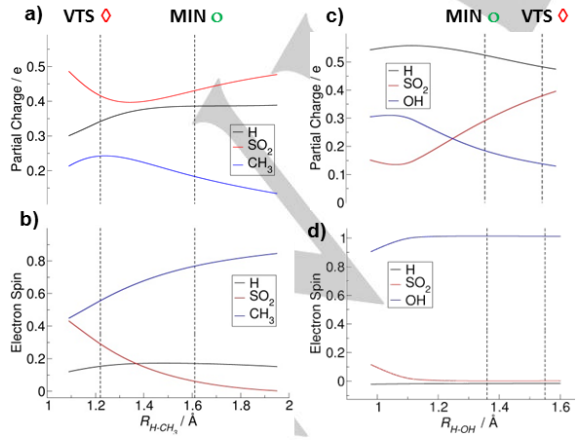


Figure 5. Partial charge and spin distribution at the B3LYP/6-31++g** level of the theory for the relevant fragments, H (black), CH_3 (blue) and SO_2 (red) involved in both the reactions of SO_2^{+} with methane (a and b, left panel) and water (c and d right panel) as a function of the reaction coordinate H-CH_3 and H-OH respectively.

In the reaction with methane (an apolar molecule, IP=12.61 eV)[19] the VTS has the charge almost equally shared between the SO_2 (+0.43 *e*) and CH_4 (+0.57 *e*) moieties while the doublet spin is 0.25 in the O of SO_2^{+}, directly involved in the interaction, and the remaining is on H (0.16) and CH_3 (0.55) of CH_4 (see the isosurfaces in Figure 4a). At the MIN structure both charge and doublet spin are almost completely separated: the charge (+ 0.79 *e*) is mainly on the newly formed species HSO_2^{+} and the spin is almost entirely localized in the CH_3 (0.82) moiety (Figure 4a). In summary, the results obtained with methane show that at the VTS, the charge and the spin are distributed in the two separated moieties SO_2 and CH_4 that interact through the H atom (Figure 5a-b). A different scenario (Figure 4b and 5 c-d) is observed in the reaction with water (a polar molecule with μ_D= 1.847 D and IP=12.62 eV)[19] where the doublet spin and the charge belong to the OH group of the still intact H_2O at the beginning of the reaction (Figure 5 c- d) while in the MIN as well as in the VTS the total spin (~1.0) and the charge (MIN=+0.82 *e*, VTS= +0.86 *e*) are localized in the newly formed OH and HSO_2^{+} species respectively (Figure 4b). It may be claimed that, despite the similar IP of the two reacting neutrals and the higher BDE of O-H in H_2O with respect to C-H in CH_4, the reaction with water proceeds without "obstacles". The higher polarity of water, its capacity to form hydrogen bonds with the oxygen of sulfur dioxide, the electronegativity of O in water higher than that of C in methane and finally, the less structural reorganization required to pass from the planar HOH to the OH radical, with respect to the one needed to change from tetrahedral CH_4 to the CH_3 planar structure are at the base of the different spin and charge distribution along the reaction path of the two systems. Hence with water, a rapid electron-proton transfer (EPT)[12c],[25] mechanism in a well interacting and connected structure $[OSO\text{-}HOH]^{\cdot+}$ is operative and clearly results in higher reaction rate constant and collision efficiency ϕ observed for this reaction. In the water case, no VTS before the minimum reduces the rate of the formation of the final products and each collision is a reactive collision, namely the experimental rate constant 2.60×10^{-9} ± 30 % $cm^3s^{-1}molecule^{-1}$ at 298 corresponds to the collision rate constant ($k_{coll}=2.60\times10^{-9}$ $cm^3s^{-1}molecule^{-1}$) obtained according to the average dipole orientation theory.[22] On the contrary, in the reaction with methane the VTS located near the reagents, with spin and charge not completely separated, produces a slowdown of the reaction, resulting in an actual rate constant lower than collision rate constant ($k_{coll}=1.03\times10^{-9}$ $cm^3s^{-1}molecule^{-1}$) and a collision efficiency lower than 100%.[11e]

The kinetic trend of the two reactions with the temperature of the reagent ion SO_2^{+} in its ionic ground state has been also investigated for the first time by calculating the temperature dependence of the rate constants (see equations (1) and (2) in theoretical section). In Table 1 some values of the

calculated *k* vs temperature (in eV and K) are reported while the whole trend of *k* in the range 12.373-12.804 eV is shown in Figure 6.The temperature scale used in the rate constants calculations has been fixed in such way that 0 K corresponds to the calculated adiabatic ionization potential of SO_2 ,IP=12.373 eV.

Table 1. Calculated values of kinetic constants vs temperature for the reaction of SO_2^+ with methane and water (at $IP_{SO2(theory)}$= 12.373 eV , T=0 K).

T (eV)	T (K)	k_{CH4}[a]	k_{H2O}[a]
12.399	298.15	6.70 (6.58)[b]	23.9 (26.0)[c]
12.416	500	1.75	19.5
12.442	800	1.36	16.4
12.459	1000	1.51	15.2
12.804	5000	19.1	9.78

[a] $x10^{-10}$ cm^3 s^{-1} $molecule^{-}1$; [b] Ref. [11e]; [c] Ref. [11f].

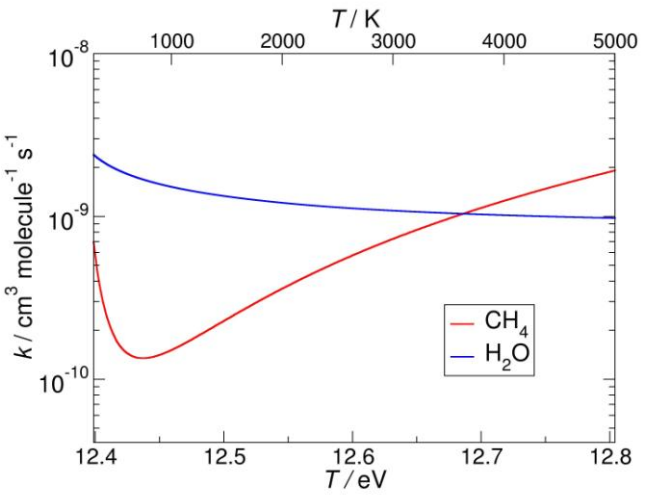


Figure 6. Calculated rate constants vs temperature (in K and eV) for the hydrogen transfer reactions of SO_2^+ with water (blue line) and methane (red line).

The theoretical results are in agreement with the experimental data. Indeed, the rate constants for both chemical reactions measured at 298.15 K overlap, within the error, with the experimental ones (Table 1), and the plot of the calculated rate constants with the temperature (Figure 6) clearly reflects the trend of ratio product/reagent obtained in our experiments at the increasing photon energy (Figure 2). The higher internal energy, distributed in its vibrational and rotational degrees of freedom in the SO_2^+ radical cation, leads to a weaker and less stable interaction between the SO_2^+ and H_2O, where the hydrogen bond plays a fundamental role. This is also true at increasing temperature: the calculated rate constants decrease but remain in the range of 10^{-9} cm^3 $s^{-1}$$molecule^{-1}$, as expected by theory. [22] In the reaction with methane the same excess energy at the very beginning does not favor the reaction, probably reducing the lifetime of the reacting complex $[SO_2\text{-}CH_4]^{\cdot+}$ so that the rate constant reduces as in the reaction with water. However at higher temperatures and internal energies the distribution of the high excess energy among the degrees of freedom in the sulfur dioxide-methane complex probably weakens the C-H bond which interacts with the O atom of SO_2, favoring its breaking and allowing the rate to increase. It is worth mentioning that in the calculation of rate constants for the reaction with methane the oscillators are considered harmonic, an approximation non valid at the very high temperature where the VTST calculations produce overestimated rate constants.

Conclusions

In this study a joint experimental and theoretical effort has been done to explore and understand the collision efficiency at 298 K and the different temperature trends obtained for the reactions of SO_2^+ radical cation with two relevant and ubiquitous molecules: H_2O and CH_4. New reaction dynamics have been obtained at different temperatures of fundamental and multidisciplinary interest as in astrochemistry. The theoretical analysis clearly explains the higher efficiency of the reaction with water than with methane, due to the polar, spin and charge effects. The VTST theory approach has been successfully applied to the reaction with an open shell, charged species, like SO_2^+ and has been demonstrated to be a powerful tool to elucidate some aspects, until now not completely clear, of methane and water activation mechanisms.

Experimental Section

The CiPo beamline at ELETTRA is equipped with an electromagnetic elliptical undulator/wiggler and a Normal Incidence Monochromator to cover the 5-40 eV energy range. The grating used for the experiment is an aluminum coated holographic spherical grating with 1200 grooves/mm (Al-NIM), that provides radiation in the range 5–17 eV with a resolving power of about 1000. The ionization region is equipped with ion optics (one planar repeller and three extractor lenses), set in front of the octupolar RF-driven ion guide. The effusive beam of the neutral precursor SO_2 (constant pressure of about 10^{-6} mbar) is introduced via a needle, in the center of the ionization region crossed at 90° by the photon beam. The ions SO_2^+ produced are transported into the octupole by the extraction optics, set perpendicularly to the propagation axis of the photon beam. The neutral reagents H_2O/CH_4 are introduced in the octupole via a needle valve which finely regulates the pressure in the range 10^{-7}-10^{-5} mbar. The octupole acts as a two-dimensional trap, which ensures an extended reaction region and an efficient collection of the ionic products of the ion-molecule reactions. A quadrupolar deflector mounted at the end of the octupole transfers the ions in the quadrupole mass spectrometer equipped with a channeltron multiplier detector (see Figure 1S for the sketch of the apparatus in SI). The collision energy, CE, is determined by measuring the SO_2^+ yield as a function of the retarding

field. In a typical experiment the yields of ionic reagent (m/z 64) and product (m/z 65) were recorded scanning the photon energy from 12 to 14 eV (energy step=200 meV and acquisition time= 30 s/point) at different fixed pressures (ranging from 10^{-6} to 10^{-5} mbar) and CE (0, 0.5 or 1.0 eV). In this photon energy range $SO_2^{\cdot+}$ precursor ion doesn't dissociate [19] as verified in our experiments carried out in absence of neutral reagent. Moreover the presence of other possible products from ion-molecule reaction has been checked acquiring the mass spectra in the range 10<m/z<100 at the photon energy hν=14.0 eV (acquisition time of 5s/point). It is noteworthy that the absence of the background water in the octupole has been verified in the experiments performed collecting the mass spectra of the SO_2^+ with background molecules at the pressure of 10^{-7} mbar. The photoionization efficiency curves of the ionized precursor and fragment ion SO^+ allowed to measure the appearance energy AE(SO^+) (Figure 2S in SI), in the absence of reacting molecules. The apparatus and the well established experimental procedure are described in detailed elsewhere. [26], [27]

Materials. All the samples were used at room temperature and for water several freeze-pump-thaw cycles have been carried out before its use. Sulfur dioxide and water were purchased from Sigma-Aldrich with a purity > 99.98% whereas methane is from SIAD with purity > 99.98%.

Theoretical Section

The description of the forces at play in the reactions involving SO_2^+ with methane or water has been based on Density Functional Theory formalism, used to explore the Potential Energy landscape involved in the reactions. The hybrid exchange-correlation functional Becke, three-parameter, Lee-Yang-Parr [28] has been adopted together with the split-valence double-zeta Pople 6-31++g** basis set with polarization and diffuse functions.[29] The reaction region of the PES has been studied by full optimizations by scanning the C-H and O-H coordinates, where the hydrogen atom is the one involved in the exchange with the O atom of the SO_2^+ ion. The scanning coordinate started at a 1.089 Å and ended at 1.609 Å, with a variable step, and generates the Minimum Energy Paths (MEP) needed to compute the reaction rate coefficients. The variational transition state theory approach, specifically suited for applications with barrierless reactions,[30] has been used to model the present reactions. The RRKM model for the TS theory, as it is well known, is based on a strong coupling of the degrees of freedom within the reactive complex adduct The ensemble of the complexes formed during the reaction, evolves in the phase-space faster than the characteristic time scale of the reaction itself; each elementary step of the reaction is in microcanonical equilibrium due to the fact that the evolution of the complex occurs uniformly. The evaluation of the rate constant is based on the calculation of the molecular partition functions of both the reagents in their minimum energy geometries and the complex in the variational transition state geometry, which is defined as the phase-space point where the molecular partition function of the complex ($Q^{\ddagger}$) itself has a minimum value This is the geometry at which the evolution of the reaction is the slowest, i.e. the bottleneck of the evolution from the reagents to the products. Hence the rate constant is

$$k(T) = S\frac{k_B T}{h}\frac{Q^{\neq}(T)}{Q(T)_{ion}Q(T)_{neutral}} \qquad \textbf{(1)}$$

where all the above partition functions are temperature dependent. The minimization of the molecular partition function of the complex along the relevant MEPs has been done at every T. The vibrational partition function has been computed using the vibrational frequencies from normal mode analysis within the harmonic approximation. The S term in equation (1) is a symmetry factor that takes into account the different equivalent, indistinguishable, ways in which the reaction can occur. This approach is meaningful when the geometry of the VTS complex is in the region between the reactants and the products as in the case of the methane molecule. On the contrary, the same approach cannot be used for the reaction with water, where the VTS geometry of the complex is in the region of the products, indicating that there is no bottleneck during the reaction, which is fast and efficient. In this case we have calculated the rate constant by using capture theory based on variational transition state theory/classical trajectory study of thermal energy ion-polar molecule collisions:[31]

$$k(T) = \begin{cases} 0.4767a(T) + 0.6200; & a(T) \geq 2 \\ \dfrac{\left(a(T)+0.5090\right)^2}{10.526} + 0.9754; & a(T) \leq 2 \end{cases} \qquad \textbf{(2)}$$

$$a(T) = \frac{\mu_D}{\sqrt{2\alpha k_B T}}$$

where, and α and μ_D are the polarizability and the dipole moment of the water molecule respectively. Ab initio calculations have been done with the Gaussian program.[32]

Acknowledgements

The work has been supported by the MIUR FIRB RBFR10SQZI project.

Keywords: rate constants • temperature • VTST • Synchrotron radiation• sulfur dioxide

[1] a) M. Larsson, W. D. Geppert., G. Nyman *Rep. Prog. Phys.* **2012**, *75*, 066901(75pp); b) S. Petrie, D. K. Bohme *Mass Spectrum. Rev.* **2007**, *26*, 258-280.

[2] a) F. Lanucara, S. W. Holman, C. J. Gray, C. E. Eyers *Nat. Chem.* **2014**, *6*, 218-294 b) P. Markush, P. Bolognesi, A. Cartoni, P. Rousseau, S. Maclot, R. Delaunay, A. Domaracka, J. Kocisek, M. C. Castrovilli, B. A. Huber, L. Avaldi *Phys. Chem. Chem. Phys.* **2016**, *18*, 16721-16729.

[3] a) R. H. Crabtree *Chem. Rev.* **1995**, *95*, 987-1007; b) G. A. Olah, A. Goeppert, G. K. S. Prakash *J. Org. Chem.* **2009**, *74*, 487-498; c) G. A. Olah *Angew. Chem. Int. Ed.* **2005**, *44*, 2636-2639..

[4] a) V. G. Anicich *J. Phys.Chem. Ref. Data* **1993**, *22*, 1469-1569; b) V. G. Anicich *Astrophys. J. Suppl. Ser.* **1993**, *84*, 215-315.

[5] a) H. Schwarz *Angew. Chem. Int. Ed.* **2011**, *50*, 10096-10115; b) H. Schwarz, *Angew. Chem. Int. Ed.* **2015**, *54* (35),10090-10100; c) M. Zhou, R. H. Crabtree *Chem. Soc. Rev.* **2011**, *40*, 1875-1884; d) J. A. Labinger, J. E. Bercaw *Nature* **2002**, *417*, 507-514.

[6] L. E. Snyder, J. M. Hollis, B. L. Ulich, F. J. Lovas, D. R. Johnson, D. Buhl *Astrophys. J.* **1975**, *198*, L81-L84.

[7] a) H. C. Huang, Y. J. Kuan, S. B. Charnley; N. Hirano, S. Takakuwa, T. L. Bourke *Adv. Space Res.* **2005**, *36*,146-155; b) K. M. Menten, F. Wyrowski, A. Belloche, R. Güsten, L. Dedes, H. S. P. Müller *Astron. Astrophys*. **2011**, *525*, A77 (15 pages).

[8] a) J. B. Marquette, C. Rebrion and B. R. Rowe *Astron. Astrophys.* **1989** *213*, L 29-L32; b) V. G. Anicich, Jr. W. T. Huntress *Astrophys. J., Suppl. Ser.* **1986**, 62, 553-672.

[9] V. Lattanzi, C. A. Gottlieb, P. Thaddeus, S. Thorwirth, M. C. McCarthy *Astron. Astrophys*. **2011**, *533*, L11 (4 pages)

[10] a) J. H. Lacy; J. S. Carr, N. J. Evans, F. Baas, J. M. Achtermann, J. F. Arens, *Astrophys. J.* **1991**, *376*, 556-560 ; b) A. C. Cheung, D. M. Rank, C. H.Townes, D. D. Thornton, W. J. Welch *Nature*, **1969**, *221* (5181), 626-628.

[11] a) V. N. Cavaliere, D. J. Mindiola *Chem Sci.* **2012**, *3*, 3356-3365; b) Z.C. Wang, T. Weiske, R. Kretschmer, M. Schlangen, M. Kaupp, H. Schwarz, *J. Am. Chem. Soc.* **2011**, *133*, 16930-16937; c) M. Yagi, M. Kaneko, *Chem. Rev.* **2001**, *101*, 21 – 35; d) G. de Petris, A. Cartoni, A. Troiani, V.Barone, P. Cimino,G. Angelini, O. Ursini *Chem. Eur. J.* **2010**, *16*, 6234 – 6242; e) G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini *Chem. Eur. J.* **2009**, *15*, 4248 – 4252.; f) G. de Petris, A. Cartoni, A. Troiani, G. Angelini,O.Ursini *Phys. Chem. Chem. Phys.* **2009**, *11*, 9976-9978.

[12] a) J.Li, X.-N. Wu, S. Zhou, S. Tang, M. Schlangen, H. Schwarz *Angew. Chem. Int. Ed.* **2015**, *54*, 12298 –12302; b) J. M. Mayer *Acc. Chem. Res.* **2011**, *44*, 36-46; c) J. M. Mayer *Annu. Rev. Phys. Chem.* **2004**, 55, 363-390.

[13] a) S. J. Blanksby, G. B. Ellison *Acc. Chem. Res.* **2003**,*36*, 255-263; b) B. Ruscic, D. Feller, D. A. Dixon, K. A. Peterson, L. B. Harding, R. L. Asher, A. F. Wagner *J. Phys. Chem. A* **2001**, *105*, 1-4; c) B. Ruscic, M. Litorja, R. L. Asher *J. Phys. Chem. A* **1999**, *103*, 8625-8633.

[14] D. G. Truhlar, B. C. Garrett *Annu. Rev. Phys. Chem.* **1984**, *35*,159–189.

[15] a) Y. X. Zhao, X. N. Li, Z. Yuan, Q. Y. Liu, Q. Shi, S. G. He *Chem. Sci.* **2016**,*7*, 4730-4735; b) X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D.Tan ,R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao *Science*, **2014**, *344*, 616-619.

[16] A. Derossi, F. Lama, M. Piacentini, T. Prosperi, N. Zema, *Rev. Sci. Instrum.* **1995***, 66*, 1718-1720.

[17] a) W-Z. Li, M.-B. Huang, B-Z. Chen *J. Chem. Phys.* **2004**, *120*, 4677-4682; b) D. M. P. Holland, M. A. MacDonald , M. A. Hayes , P. Baltzer, L. Karlsson, M. Lundqvist, B. Wannberg, W. von Niessen *Chem. Phys.* **1994**, *188*, 317-337; c) L. Wang, Y. T. Lee, D. A. Shirley *J. Chem. Phys.* **1987**, *87*, 2489-2497.

[18] B. Brehm, J.H.D. Eland, R. Frey, A. Küstler *Int. J Mass Spectrom. Ion Phys.* **1973**, *12*, 197-211.

[19] NIST Chemistry WebBook, NIST Standard Reference Database number 69, June 2005, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg MD), 20899 http://webbook.nist.gov.

[20] C. Lévêque, H. Köppel, R. Taïeb *J. Chem. Phys.* **2014**, *140*, 204303, (11 pages).

[21] G. Dujardin, S. Leach *J. Chem. Phys.* **1981**, *75*, 2521-2531.

[22] M. T. Bowers *Gas Phase Ion Chemistry*, *Vol. 1* Accademic Press, New York **1979**

[23] a) F. A. Gianturco, M. Satta, M. Mendolicchio, F. Palazzetti, A. Piserchia, V. Barone, R. Wester*, Astrophys. J.*, **2016**, *830*:2 (10 pages); b) F. Carelli, F. A. Gianturco, R. Wester, M. Satta *J Chem. Phys.* **2014**, *141*, 054302 (10 pages).

[24] A. A. Fokin, P. R. Schreiner *Chem. Rev.* **2002**, *102*, 1551-1593.

[25] J. J. Warren, T. A. Tronic, J. M. Mayer *Chem. Rev.* **2010**,*110*, 6961-7001;b) C. Costentin, D. H. Evans, M. Robert, J.M. Saveant, P. S. Singh *J. Am. Chem. Soc* .**2005**,*127,* 12490-12491.

[26] M. C. Castrovilli, P. Bolognesi, A. Cartoni, D. Catone, P. O'Keeffe, A R Casavola,S. Turchini, N. Zema, L. Avaldi *J. Am. Soc. Mass Spectrom.* **2014**, *25*, 351–367.

[27] M. Satta, P. Bolognesi, A. Cartoni, A R Casavola, D. Catone, P. Markus, L. Avaldi *J. Chem. Phys.* **2015**, 143, 244312, (8 pages).

[28] a) A.D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648-5652; b) C. Lee, W. Yang, R.G. Parr *Phys. Rev. B* **1988**, *37*, 785-789; c) S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58,*1200-1211;d) P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623-11627.

[29] a) P.C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213-222; b) M.M. Francl, W.J. Petro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654-3665.

[30] A. Fernández-Ramos, J. A. Miller, S. J. Klippenstein, D. G. Truhlar *Chem. Rev.* **2006**, *106,* 4518-4584.

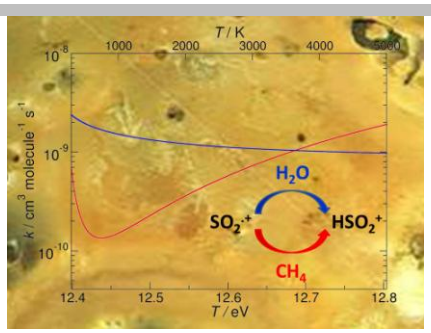
[31] T. Su, W. J. Chesnavich *J. Chem. Phys*. **1982**, *76*, 5183-5185.

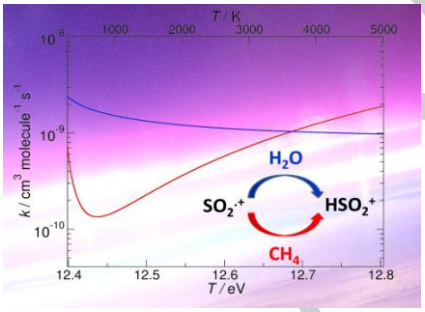
[32] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

FULL PAPER

Text for Table of Contents

The sulfur dioxide radical cation efficiently reacts with water and methane with opposite temperature-dependent kinetic trend. The experiments with tunable synchrotron radiation show only one product: HSO_2^+. Theory explains the results by means of the polar, spin and charge effects as well as structural reorganization occuring in the reaction coordinate.





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HSO_2^+ formation from ion-molecule reactions of $SO_2^{\cdot+}$ with water and methane: two fast reactions with reverse temperature-dependent kinetic trend