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Review on The C + CH^+ Scattering

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Abstract: The scattering processes of the astrophysical relevant collision of C with $CH^+$is reviewed here. The scattering of C + $CH^+$is an exothermic processes leading to the formation of another astrophysically important species C_2^+. The minimum energy path leading from reactant to product proceeds through a steep downhill path via a deep potential well of ~ 6.7 e V.

Understanding the chemistry of the interstellar medium (ISM) is concealed subject till to date. The bimolecular collision of atom and molecule, ion with molecule and atom with molecular ion are proposed to have acrucial roll in the chemistry of interstellar medium as well as in the chemistry of early universe[1-2].Thegas phasebimolecular collision of atomic C with the CH^+ is an important astrochemical processes involving carbon and hydrogen atoms and is crucial partner for evolution of carbon chemistry in the ISM[3].

In the ISM, carbon may exist in both atomic and ionic forms andis the backbone of a wide variety of species available in the interstellar gas phase e.g. CO, polycyclic aromatic hydrocarbon, hydrogenated amorphous carbon, carbon dusts, diamond, etc.[4-6].

The abundance of carbon and its cation into the galaxy is primarily because of the dying stars in the asymptotic giant branch (AGB) and supernova explosions (SNe)[7]. They are also produced inside the stars during helium burning through the triple-alpha reaction [8].

The CH+ is ubiquitous throughout the interstellar clouds and its large abundances naturally makes is a potential target for the three body collisions [9].

A chemical reaction through bimolecular collision at ISMmodifies the chemical composition of ISM. C + CH^+ reaction is proposed to be one of the important ion-molecule reactions for the production of hydro carbons in interstellar clouds[3] and also is prototype model reaction for the carbon-carbon chemical bondformation. Never the less the above collision includes two important species methylidyne cation CH^+ and dicarbon cation C_2^+.Alike CH^+,the dicarbon cation $C_2^+$is also an important component of the ISM and is detected in Halley comet [10] and in Giacobini-Zinner comet [11] by the mass-spectroscopic sampling.

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To have a better understanding of the chemistry of the ISM involving carbon and hydrogen (or hydrocarbon), a lot of studies has been done both experimentally and theoretically. [12-14 and references therein]

Very recently a series of theoretical studies has been carried out by Rampino et. al. to simulate the reaction dynamics of $CH^+$with C [12-14]. The study of the author revel that reaction of C and CH^+ on its ground state is exoergic and proceeds in the following pathway

$$C(^3P_0) + CH^+ (X\ ^1\textstyle\sum^+) \rightarrow C_2^+(X\ ^4\textstyle\sum_g^-) + H\ (^2S_{1/2})\ .$$

This paper reviewed the collisional dynamics and potential energy surface for the C + CH^+ scattering. Because of its potential role in the chemistry of diffused cloud the study of scattering dynamics for the titled reaction got some attention from the researcher.

The occurrence of the titled reaction in the astrophysical environment was initially predicted by Solomon et.al.[2]. They predicted that the bimolecular collision of CH^+ with C leads to the formation of C_2^+. The rate constant for this reactions is also estimated by them as 1×10^{-9} $cm^3s^{-1}$by using Langevin capture model.Prasad et al. [15] estimated the rate to be 1.2×10^{-9} $cm^3\ s^{-1}$. Recently Chabot et al. [16]had proposed that the collision of C + CH^+ leads to C_2^++ H (95%) and C_2 + H^+ (5%) byperforming semi empirical calculations. The rate of formation of C_2^+ is assumed to followmodified Arrhenius equation $k(t) = \alpha\left(\frac{T}{300}\right)^{\beta} e^{-\frac{\lambda}{T}}$, and $\alpha = 1.14 \times 10^{-9}$ $cm^3\ s^{-1}$and $\beta=0$ is estimated by these authors.

The very first step for an understanding of the molecular dynamics is to understandthe potential energy surfaces(s) (PES(s)) of the colliding system. Basicallyit describes the potential energy which is an electrostatic interaction betweennuclei and electrons involved in the reaction as a function of nuclear coordinate.The one asymptote of the PES describes the reactants and the other asymptoteto products. The gradient at any point on the PES describes the force felt bythe atom and/or molecule in that point during chemical transformation fromreactants to products.

Potential energy Surface:

Despite having 6 electrons the electronic structure calculations of C_2H^+ is very complicated. The study of Krishnan et al. [17] and Frenking et al. [18] revels that the groundelectronic state of the triatomic species is $^3\Pi$and the minimum energy occurs in the colinear CCH^+ geometry. Very recently Pacifici et al [12–14] has proposed an abinitio potential energy surfacefor the reaction C + CH^+. This PES was further utilised by those authors to estimate the reaction rate constant as a function of temperature.

The Born -Oppenheimer PES was computed by a high-performance computing technique (HPC) using the grid-empowered molecular simulator (GEMS) method [12]. In this method, the dynamics is calculated in a four step processes.

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The very first step of the processes is to calculate the abinitio energy at different nuclear geometry. The basis set and level of theory applied to calculate the abinitio points are Atomic-natural-orbital relativistic-correlation-consistent(ANO-RCC) basis set and a second-order multi-referenceperturbation theory (MRPT) in the "partially contracted"PC-NEVPT2 approach [19-20] usingcomplete-active-space self-consistenteld (CASSCF) reference wavefunctions, respectively. The scalar relativistic effects were accounted elegantly by using Douglas-Kroll-Hess Hamiltonian [21].

The choice of nuclear geometry at which abinitio points have to be calculated is another crucial step. This was carried out by space-reducedbond-order (SRBO) grid approach of Rampino [14].

A total of 775 abinitio points was computed for the C_2H^+ system. 10 abinitio points was calculated for each of the diatomic system CH^+ and C_2^+.

The second step is to fit the data to a set of mathematical functions. The global analytical potential energy surface is fitted by fitting the 775 triatomic abinitio points by using thegfit3c code of Aguado-Paniagua[22] . The root-mean-square (rms) deviation of the fitteddata with abinitio data set is 1×10^{-1} eV.

Salient features of the PES:

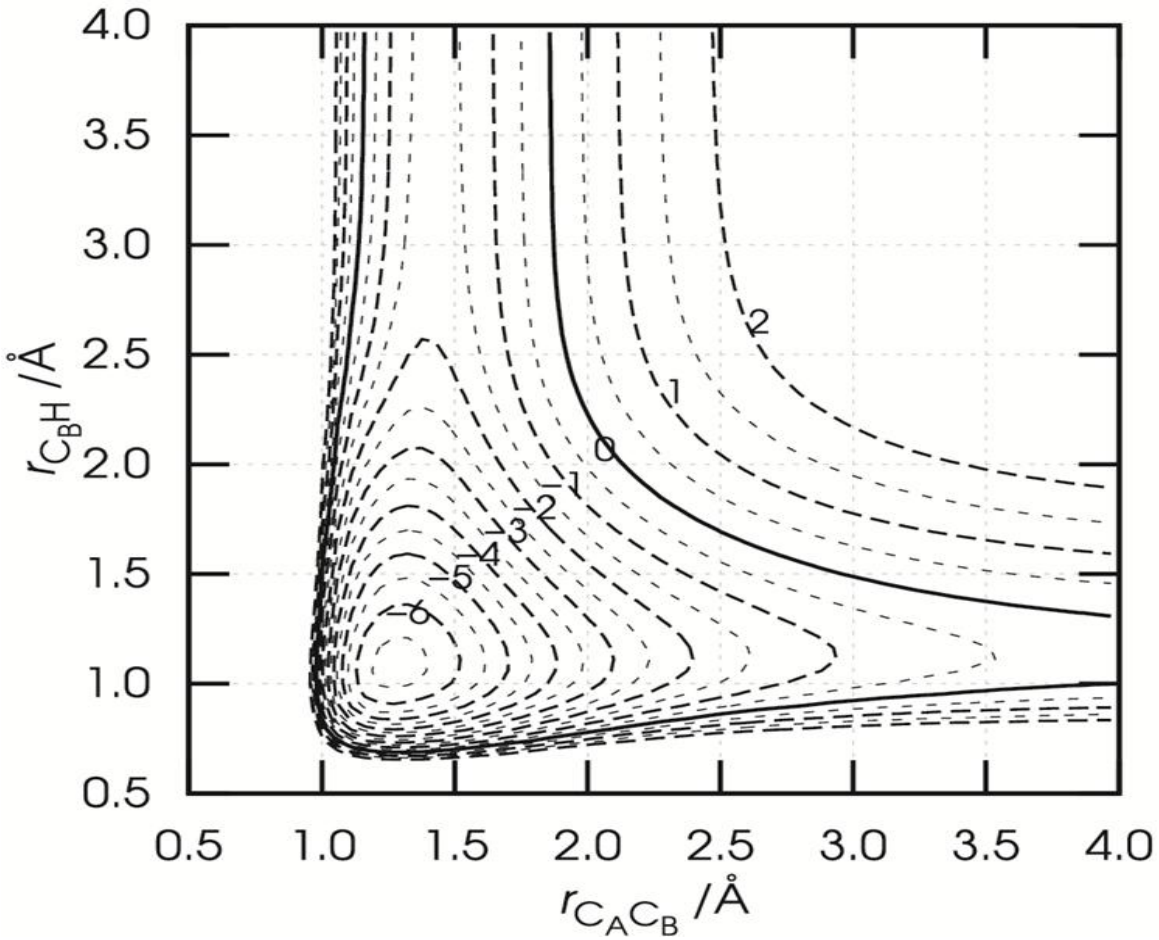

Fig 1: Potential Energy Surface cuts of the $C + CH^+ \rightarrow C_2^+ + H$

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The collisional process of C + CH^+→ C_2^++ H is exoergic by 1.65eV. Presence of a deep potential well of around 6.7eV is reported for this reactive system. A minute study of the PES revels that the global minima arises at collinear geometry of $[C\text{-}C\text{-}H]^+$and at internuclear distance at R_{C_C}= 1.28Å, R_{C_H} = 1.08Å. It is also evidenced that the triatomic dissociation energy lies above 10.79 eV to that of global minima. A contour diagram of the PES is shown in the figure 1. The existence of deep well in the interaction region is evidenced.

This PES is then utilised by the authors to determine the dynamical properties by applying the quasi classical trajectory (QCT) method as implemented in VENUS96[22] and also by a moleculardynamics method as implemented in the Ring Polymer Molecular Dynamics (RPMD) technique[14]. Thermal rate coefficients, state-specific ratecoefficients, and cross sections for this reaction are estimated.

In the QCT method a large number of classical trajectories are calculated by solving the Hamilton equation of motions and at the end of the evaluations, the speciesproduced are identified. Based on the product formed the channels are identified as reactive, non-reactive or dissociative channel. Then, the reaction cross section is estimated by:

$$\sigma = \pi\, b^2 \frac{N_r}{N},$$

where, N and Nr indicates the total number of trajectories and the total number of reactive trajectories, respectively, and b is the maximumvalue of the impact parameter leading to reaction. The thermal rate constant is then calculated by the authors by taking a statisticalaverage of the cross-sections in the following way,

$$k(t) = \sigma(v) = \sqrt{\frac{8k_B T}{\pi\mu}}\,\sigma\,,$$

where,$k_B$and T represent the Boltzmann's constant and the reduced mass of the reactants, respectively.

Dynamical Observations: It was observed that the rate of the reaction initially increases with increasing temperature. The Rate of the reaction reaches a maximum at some optimum temperature of ~420K and then decreases steadily with increasing temperature. A comparative study of the rate constant obtained from QCT methods are shown in the figure 2. It is also observed that the rovibrational excitation of the reagents decreases the reactivity. To have a further analysis of the reagent rovibrational excitation, initial state specific cross sections are calculated. It was observed that the cross section decreases with increasing collision get converged at some high collision energy. In other word, both the internal and external excitation of the reagent causes a reduction in the reactivity. A comparison between the QCT and the molecular dynamics methods shows some

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significant deviations of the results at the low collisional energy. The deviations in the dynamical outcome indicates the necessity of a full quantum mechanical treatment of this reactive system as at low temperature region the dynamics may be dominated by quantum effect.

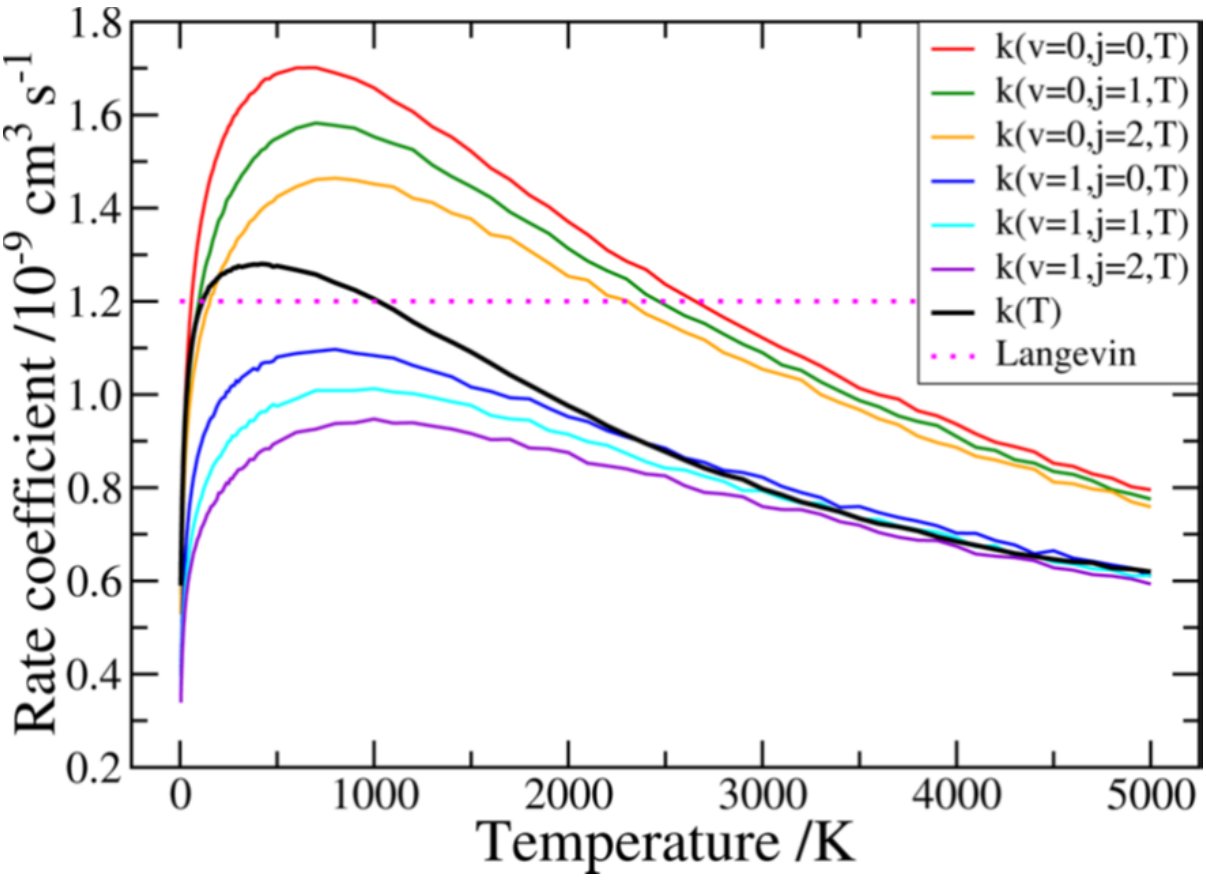

Fig 2: Initial state selected as well as state specific rate constant is plotted as a function of temperature.

Conclusion: An astrophysically important reactive system, C + CH^+ collisional processes, is reviewed here. The global potential energy surface, the crucial stationary points on the PES and mechanistic details of the reaction dynamics along with collisional outcome is review in this work.

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