

Destruction of interstellar methyl cyanide (CH_3CN) via collisions with He^+ ions

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ABSTRACT

Context. CH_3CN (methyl cyanide) is one of the simplest and most abundant interstellar complex organic molecules (iCOMs), and has been detected in young solar analogues, shocked regions, protoplanetary discs, and comets. CH_3CN can therefore be considered a key species to explore the chemical connections between the planet-forming disk phase and comets. However, for such comparison to be meaningful, kinetics data for the reactions leading to CH_3CN formation and destruction must be updated.

Aims. Here we focus on the destruction of methyl cyanide through collisions with He^+ . We employed a combined experimental and theoretical methodology to obtain cross sections (CSs) and branching ratios (BRs) as a function of collision energy, from which we calculated reaction rate coefficients $k(T)$ in the temperature range from 10 to 300 K.

Methods. We measured CSs and BRs using a guided ion beam setup, and developed a theoretical treatment based on an analytical formulation of the potential energy surfaces (PESs) for the charge exchange process. The method employs a Landau Zener model to obtain reaction probabilities at crossings between the entrance and exit PESs, and an adiabatic centrifugal sudden approximation to calculate CSs and $k(T)$, from subthermal to hyper-thermal regimes.

Results. $k(T)$ and experimental BRs differ from those predicted from widely used capture models. In particular, the rate coefficient at 10 K is estimated to be almost one order of magnitude smaller than what is reported in the KIDA database. In addition, the charge exchange is completely dissociative and the most abundant fragments are $\text{HCCN}^+/\text{CCNH}^+$, HCNH^+ and CH_2^+ .

Conclusions. Our results, combined with a revised chemical network for the formation of CH_3CN , support the hypothesis that methyl cyanide in protoplanetary discs could be mostly the product of gas-phase processes rather than grain chemistry, as currently proposed. These findings are expected to have implications in the comparison of the abundance ratios of N-bearing molecules observed in discs with cometary abundance ratios.

Key words. astrochemistry – molecular data – molecular processes – stars: formation – ISM: molecules

1. Introduction

Methyl cyanide (CH_3CN), also known as acetonitrile or cyanomethane, is a species of great astrochemical interest among interstellar complex organic molecules (iCOMs), as it has been routinely detected in several regions of the interstellar medium (ISM) at different stages of star formation. Its first detection dates back to 1971, when some rotational lines were reported towards Sagittarius B (Solomon et al. 1971) and, since then, it has been detected towards dark clouds (Matthews & Sears 1983), diffuse and translucent clouds (Thiel et al. 2017; Liszt et al. 2018; Thiel et al. 2019), massive star-forming regions (Purcell et al. 2006), and the Galactic centre (Zeng et al. 2018). Focusing on young solar analogues, CH_3CN has been observed in Class 0 and I hot corinos (Cazaux et al. 2003; Taquet et al. 2015; Yang et al. 2021; Bianchi et al. 2022; Ceccarelli et al. 2023), in shocked

regions (Codella et al. 2009), and in planet-forming discs, where it was first detected in 2015 (Öberg et al. 2015). Subsequently, it was routinely observed in a series of surveys of protoplanetary discs (Bergner et al. 2018; Kastner et al. 2018; Loomis et al. 2018, 2020; Ilee et al. 2021). CH_3CN has also been detected in comets (Mumma & Charnley 2011), including towards comet 67P/Churyumov-Gerasimenko in the context of the ESA-Rosetta mission (Le Roy et al. 2015; Biver & Bockelee-Morvan 2019; Altwegg et al. 2019; Haenni et al. 2021).

Nitriles have a strong prebiotic relevance because they are key intermediates in the formation of biomolecules such as amino acids and RNA precursors via reaction with water in a multi-step synthesis (Sutherland 2017). For this reason, the presence of nitriles and water in comets, with CH_3CN ranging from ~0.008 to 0.054% with respect to water (Öberg et al. 2015; Biver & Bockelee-Morvan 2019), is of particular interest and makes CH_3CN a key species with which to explore the chemical connections between protoplanetary discs and comets. However, for such comparison to be meaningful, astrochemical network

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databases such as KIDA (Wakelam et al. 2015) and UMIST (Millar et al. 2024) require accurate data on the reaction rates and branching ratios (BRs) for the various CH_3CN formation and destruction pathways.

Historically, two main formation mechanisms for methyl cyanide have been proposed, one proceeding via grain-surface reactions and the other operating in the gas phase. The dominant grain-surface mechanisms are the ice-mediated $\text{CH}_3 + \text{CN}$ association reaction and the hydrogenation of C_2N on the ice surface (Garrod et al. 2008), while the radiative association reaction between CH_3^+ and HCN represents the main formation route in the gas phase (Ceccarelli et al. 2023). The network of gas-phase formation routes of CH_3CN has recently been extensively revised and updated (Giani et al. 2023), confirming the importance of the radiative association process and proposing new gas-phase formation routes, such as $\text{CH}_3\text{OH}_2^+ + \text{HNC}$, $\text{CH}_3\text{CNH}^+ + \text{e}^-$ and $\text{CH}_3\text{CNH}^+ + \text{NH}_3$.

In addition to interactions with photons and electrons (Mezei et al. 2019), the destruction mechanisms of CH_3CN are expected to be dominated by collisions with energetic ions, such as H^+ , H_3^+ , HCO^+ and He^+ . While the reactions of H_3^+ and HCO^+ lead mostly to non-dissociative proton transfer (see the results of room temperature experiments in Mackay et al. (1976); Liddy et al. (1977) and the proposed rates in KIDA (Wakelam et al. 2015) and UMIST (Millar et al. 2024) databases), collisions with H^+ and He^+ are mostly destructive. This is because, for these species, the reactivity is dominated by highly exothermic charge transfer (CT) processes, thereby enabling dissociation.

In the case of He^+ this is due to the large difference between the recombination energy of He^+ and the ionization energy (IE) of CH_3CN , of namely 12.39 eV. Collisions with He^+ have been proposed as important pathways for the decomposition of iCOMs ranging from CH_3OCH_3 and HCOOCH_3 (Cernuto et al. 2017, 2018; Ascenzi et al. 2019) to CH_3OH (Richardson et al. 2022). However, for CH_3CN , while the reaction with H^+ has been experimentally studied at room temperature (Liddy et al. 1992; Wakelam et al. 2015; Millar et al. 2024), to the best of our knowledge, no previous experimental or theoretical studies have been carried out for the reaction with He^+ , with the rates and BRs reported in the aforementioned astrochemical databases referring to predictions from capture models and chemical intuition.

From a more general perspective, barrierless elementary chemical processes (mostly driven by ions, radicals, and/or atoms and molecules in long-lived, electronically excited states; e.g. Penning processes) can occur under both sub-thermal conditions, such as those present in cold interstellar environments, and hyper-thermal conditions occurring in natural and laboratory plasmas, flames, and combustion processes. The detailed characterisation of such processes is relevant not only for fundamental studies, but also for applications well beyond the context of astrochemistry. Ion-molecule studies can employ a wide range of experimental methods (from guided ion beams and ion traps (Dohnal et al. 2023) to the Rydberg-Stark merged-beam approach (Martins et al. 2023; Hahn et al. 2024) and innovative techniques based on the use of Coulomb crystals (Voute et al. 2023; Kilaj et al. 2023; Ploenes et al. 2024; Xu et al. 2024; Krohn et al. 2023; Krohn & Lewandowski 2024)) to measure either partial and total reactive cross sections (CSs) as a function of collision energy, or rate constants ($k(T)$) as a function of temperature over a wide temperature range.

In this paper, we report partial and total $\text{He}^+ + \text{CH}_3\text{CN}$ reactive CSs measured as a function of collision energy over a range of around three orders of magnitude (from a few tens up to more

than 10^4 meV). The analysis of experimental results, carried out by a synergistic theoretical framework, exploits an adiabatic centrifugal sudden approximation for the capture dynamics of reagents in the entrance channels (Clary 1990; Pirani et al. 2006) and assumes that reactivity is triggered by non-adiabatic effects occurring at the crossings between entrance and exit channels and described within a Landau Zener treatment.

The analytical formulation of the potential energy surfaces (PESs) for both the entrance and exit channels, combined with the treatment of collision dynamics, enables the prediction of CSs and $k(T)$ across a range of conditions, from sub-thermal to hyper-thermal.

Results from experiments probing the dynamics of reactive collisions, as in the present work, represent crucial tests for the simple or approximate methods often employed to describe reaction probabilities of ion-molecule processes occurring under sub-thermal conditions. In particular, capture theory predictions, determined exclusively by the strength of long-range attraction, are likely to overestimate the value of the rate coefficients in all cases where the short-range part of the interaction potential is important, such as in the presence of crossings between multiple nearby PESs or when the dynamics is not adiabatic (Tsikritea et al. 2022). Therefore, for realistic estimates of kinetic rate constants and product BRs, to be used in the modelling of various processes of relevance not only in astrochemistry but also in other fields such as industrial and laboratory plasmas, it is necessary to derive the underlying PESs and to properly describe the collision dynamics. Finally, as emphasised by the present investigation, the comparison of calculations with experimental results is essential to test and eventually refine the accuracy of theoretical models.

Section 2 summarises the basic details of the adopted experimental technique, while Section 3 provides the framework of the theoretical methodologies. Section 4 details the results obtained, and their analysis, discussion, and relevance for astrochemical modelling. Conclusions follow in Section 5.

2. Experimental methodology

The experimental data presented here were collected using the GEMINI (Gas-phase Experiment for Measurements on Ion-Neutral Interactions) setup at the University of Trento. GEMINI is a tandem mass spectrometer composed of two octapoles (O) and two quadrupole mass filters (Q) in a O–Q–O–Q configuration that allows the investigation of bimolecular reactions of mass-selected ions. A scheme of the experimental setup is shown in Figure 1 and further details can be found in Ascenzi et al. (2007); Franceschi et al. (2007). Total, σ_T , and partial CSs, as well as BRs, were recorded as a function of the collision energy in the centre of mass (CM) frame (E) by measuring the yields of both parent and product ions.

He^+ ions are produced in the ion source chamber ("Source (EI)" in the figure) by electron ionisation (electron energies in the 70–80 eV range) of He, which is introduced at pressures of $\sim 10^{-6}$ mbar. Following ionisation, ions pass through the first octopole (OCT1), which acts as an ion guide, before being mass selected by a first quadrupole mass filter (QM1). Reactions occur in the second octopole, which is surrounded by a scattering cell (OCT2). Here, a $\sim 1\%$ mixture of CH_3CN in He has been chosen as the neutral reactant in order both to stabilise the vapour pressure of CH_3CN and to keep any secondary reaction(s) at a reduced level. Parent and product ions are mass selected by a second quadrupole mass filter (QM2) and

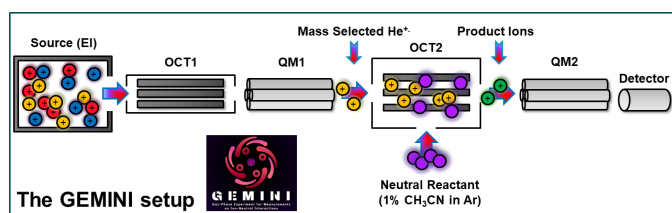


Fig. 1. Scheme of the GEMINI setup used to measure CSs and BRs for the reaction of He^+ with methyl cyanide. See the text for a detailed description.

detected by a discrete-dynode electron multiplier (Detector). The mixture is introduced at variable pressures in the range of 1.0×10^{-8} to 1.3×10^{-4} mbar, which is monitored by a spinning rotor gauge (SRG2 MKS Instruments, MA. USA).

The collision energy in the laboratory frame is dependent on both the reagent ion charge (+1 in the case of this work) and the difference between the ion source and reaction cell potentials. The retarding potential method (Teloy & Gerlich 1974) was employed to determine the maximum of the first derivative of the reagent ion yield, which defines the zero of the kinetic energy. In this way, we estimated an average reagent ion beam full width at half maximum (FWHM) of ~ 1 eV in the laboratory frame, which is equivalent to ~ 0.9 eV in the center-of-mass (CM) frame. By varying the potentials of the second octopole and all subsequent optics, we are therefore able to scan a collision energy in the CM frame (E) in the range from ~ 0.03 to ~ 10 eV.

3. Theoretical methodology

3.1. The interaction potential formulation

We constructed the PESs governing the dynamics of the reagents (entrance channel) and the products (exit channel) using a well-established phenomenological approach previously applied to a large variety of systems (Cernuto et al. 2017, 2018; Ascenzi et al. 2019; Marchione et al. 2022; Richardson et al. 2022; Falcinelli et al. 2023; Giani et al. 2023). The PESs, given in analytical forms, are a function of R (defined as the distance between He^+ and the centre of mass of CH_3CN in the entrance channel, and as the distance between He and the centre of mass of CH_3CN^+ in the exit channel) and the relative orientation of the reaction partners. It should be noted that CH_3CN is a symmetric top rotor exhibiting rotational components both along and perpendicular to its C_{3v} symmetry axis, where its high permanent electric dipole of 3.919 D (Russell 2020; Hellwege & Hellwege 1974) is aligned. In the present case, to simplify the representation of the PESs, CH_3CN is treated as a linear molecule composed of three moieties: the C and N atoms of the cyano group and an effective atom with the mass and polarisability of a methyl group. Hence, the relative orientation of the reacting partners depends only on θ , the angle formed by the $\mathbf{R}$ vector and the C_{3v} symmetry axes of CH_3CN (taken as the z axis), and the PES values are independent of the ϕ angle. The top left panel of Figure 2 depicts the adopted coordinate system for the formulation of the PESs.

Our approach identifies and describes the primary interaction components by exploiting empirical or semi-empirical formulas defined by a limited number of parameters related to fundamental properties of the interacting partners. These include the electronic polarisability (which can be partitioned into atomic and group components), ionisation potential, electron affinity, permanent charges, anisotropic charge distribution, and the shape and energy of the atomic and molecular orbitals involved in the electron transfer.

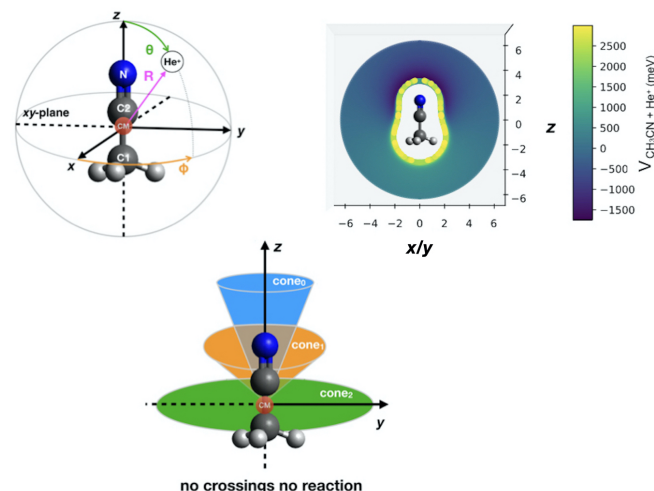


Fig. 2. Coordinate systems, PES representation and angular cones. *Top left:* coordinate system used for the description of the $\text{He}^+ + \text{CH}_3\text{CN}$ interaction. Due to the cylindrical symmetry of CH_3CN and CH_3CN^+ (in our formulation, where the CH_3 group is treated as a single effective atom), the PES (as for an atom-linear molecule system) depends solely on the polar coordinates R and θ . *Top right:* 3D representation of the PES, in the xz (or yz) plane, in the entrance channel. The attractive and repulsive contributions are indicated in blue and yellow, respectively. *Bottom:* representation of the three different angular cones cone_i (with $i = 0, 1, 2$) used in the reaction dynamics treatment discussed in Sect. 4.4.

The interested reader is referred to Mancini et al. (2024) for details of the PESs, including the values of the above-mentioned parameters. Here, we only highlight the importance of an analytical formulation of the PESs, which allows the identification of a series of crossings between entrance and exit channels, where the reactive process is promoted by non-adiabatic couplings triggered by charge transfer effects. Such crossings typically occur at shorter intermolecular distances than those where the centrifugal barrier is at a maximum. The largest uncertainty in the characterisation of the crossing positions has been estimated to be about $\pm 10\%$, taking into account the uncertainties in the PES parameters and in the value of the asymptotic energy of the exit channel (see below and Sect. 4.3). It should be noted that, while they form the basis of our theoretical treatment, the presence of crossings is not considered in classical capture models. Figure 2 (top right panel) presents a 3D representation of the entrance channel PES. This visualisation highlights the significant interaction anisotropy, which plays a crucial role in the stereo-dynamics of reagents within the entrance channels, as discussed in Sect. 3.2.

3.2. Reaction dynamics treatment

The reaction dynamics are treated within the adiabatic centrifugal sudden approximation, where the centrifugal component arising from the relative motion of the collision partners is considered as an average (diagonal) term in the interaction potential formulation used in the calculation of CSs. Cuts of the strongly anisotropic PESs, performed at defined orientation angles of the interacting partners, provide effective adiabatic PE curves that are useful for visualising, at each orientation, the crossings between entrance and exit channels.

The transition probability at the crossing points between the entrance and exit PE curves is treated by adopting a similar strategy to that used in previous investigations (Cernuto et al. 2017, 2018; Ascenzi et al. 2019; Richardson et al. 2022). In particular,

only those crossings between the entrance and exit channels that are energetically accessible will be considered as contributing to the reaction probability. Such crossings are localised in the attractive region of the entrance channel and the non-adiabatic transition probability is evaluated within the Landau–Zener–Stückelberg approach (Landau 1932; Zener 1932; Stückelberg 1932; Nikitin 1999; Nikitin & Umanskii 2012). Exploiting the simplicity of this treatment, we were able to carry out CSs calculations from sub-thermal (a few meV) to hyper-thermal (10^4 meV) collision energies (E). Specifically, the probability p_i of diabatic passage through the i -th crossing between cuts of the PESs, represented by two PE curves (at a fixed θ orientation angle), is given by:

$$p_i(E, \theta, l) = \exp\left(\frac{-2\pi \cdot H_i^2(R_i, \theta)}{\hbar \cdot v_R(l, E) \cdot \Delta_i}\right), \quad (1)$$

where E and l are the collision energy and the orbital angular momentum quantum number of the complex formed by the reagents, respectively, $H_i(R_i, \theta)$ represents the non-adiabatic coupling at the i -th crossing between the two PE curves, obtained at a specific angle θ , and Δ_i is the difference in slope between the entrance and exit curves evaluated at the value of the R coordinate at the crossing $R = R_i$. The radial velocity, v_R , describing the approach of the reagents, is defined as

$$v_R^2 = \frac{2}{\mu} \left[E \left(1 - \frac{l(l+1)}{k^2 R_i^2} \right) - E_i \right], \quad (2)$$

where E_i represents the interaction energy at the crossing point ($R = R_i$) that needs to be evaluated with respect to the asymptotic energy state of the reagents. Also, μ is the reduced mass of the $\text{He}^+ - \text{CH}_3\text{CN}$ system and k is the wavenumber defined as $k = \frac{\mu \cdot v_R}{\hbar}$. Following the guidelines given in the literature (Olson et al. 1971; Gislason & Sachs 1975; Pirani et al. 2000; Candori et al. 2001), $H_i(R_i, \theta)$ has been formulated as

$$H_i(R_i, \theta) = A \cdot R_i \cdot \left(1 + P_2(\cos \theta) \right) \cdot e^{-\alpha R_i}, \quad (3)$$

where $P_2(\cos \theta)$ is the second-order Legendre polynomial. The parameter α , depending on the IE and electron affinity (EA) of reagents comprising an electron donor (CH_3CN) and an electron acceptor (He^+), is assumed here to be equal to $2.50 \text{ \AA}^{-1}$ (Pirani et al. 2000). Therefore, only the pre-exponential A value has been adjusted in order to reproduce the energy dependence of the total integral reactive CS, $\sigma_T(E)$, which has been measured experimentally (see Sect. 4). The obtained A value is $2.0 \times 10^5 \text{ meV}$, with an estimated uncertainty of $\pm 10\%$.

At each orientation angle θ , the contribution to the total integral CS for the charge transfer evaluated at a given E value is considered as a sum of contributions from each l value:

$$\sigma(E, \theta) = \frac{\pi}{k^2} \sum_{l=0}^{l_{\max}} (2l+1) \cdot P_i(E, \theta, l), \quad (4)$$

where the formation probability of $\text{CH}_3\text{CN}^{+*}$, $P_i(E, \theta, l)$, is expressed in terms of the previously defined $p_i(E, \theta, l)$:

$$P_i(E, \theta, l) = (1 - p_i(E, \theta, l)) \cdot (1 + p_i(E, \theta, l)). \quad (5)$$

Moreover, $l_{\max}$ represents the maximum value of l for which the system is able to reach the crossing point by overcoming the

centrifugal barrier in the entrance channel. For high collision energies, this is always the case and $l_{\max}$ is given by

$$l_{\max} = kR_i \sqrt{1 - \frac{E_i}{E}}, \quad (6)$$

which represents the maximum value of l for which v_R is real at the i -th crossing point.

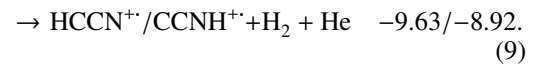
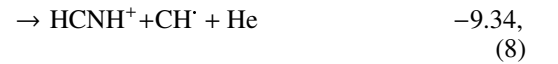
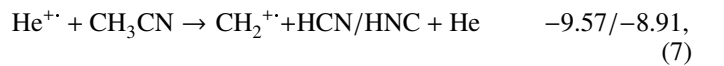
4. Experimental results and theoretical implementation

4.1. Experimental results: BRs and comparisons with other ionisation methods for CH_3CN

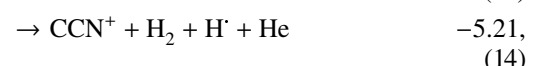
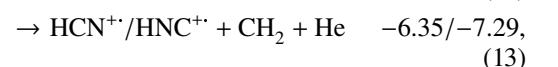
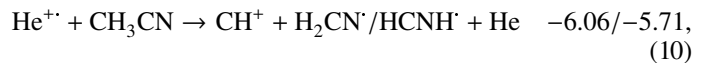
The main ionic products of the reaction of He^+ with CH_3CN are those at m/z 14, 28, and 39, while less intense products are observed at m/z 13, 15, 27, 38, and 40. Notably, as we do not observe a product at m/z 41, corresponding to the formation of CH_3CN^+ , we conclude that the electron-transfer process is completely dissociative. However, we do note additional peaks at m/z 42 and, though less intense, at m/z 54, which are identified as products of secondary reactions of the most prominent primary ions with excess CH_3CN .

The extent of secondary reactions has been minimised by using a mixture of CH_3CN diluted with He, but it was impossible to completely eliminate secondary reactions due to the high reactivity of CH_3CN (having a large proton affinity of 8.076 eV (Linstrom & Mallard 2024)) with many hydrocarbon and N-containing hydrocarbon ions via proton transfer. The presence of secondary reactions in ion reactivity studies with CH_3CN has been noted previously using quite different experimental setups (Krohn et al. 2021, 2023).

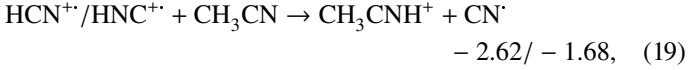
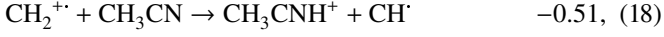
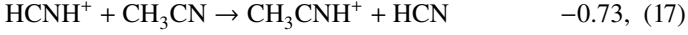
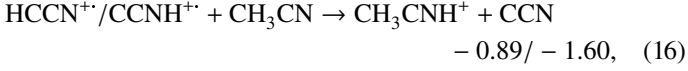
The assignments for the observed major primary products and their corresponding reaction energetics, that is, ΔH° (298 K) given in eV as calculated from available literature data (Ruscic & Bross 2020; Linstrom & Mallard 2024), are as follows:



Similarly, the assignments for the observed minor primary products are as follows:



Finally, the secondary reactions giving products at m/z 42 and m/z 54 are identified as:



As the secondary product at m/z 42 (CH_3CNH^+) can come from more than one primary reactant ion, the different reaction rates for the respective secondary processes must be considered in order to obtain accurate BRs for the various primary reaction channels.

For reaction (16), rates in the literature are in the $3.00\text{--}3.54 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ range (Franklin et al. 1966; Vogt & Beauchamp 1975; Anicich 2003), with the main channel being proton transfer (Gray 1968; Wincell et al. 1988). For reactions (17) and (18), the proton transfer process is the only observed channel, with reported rate constants of $3.80 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (McEwan et al. 1989) and $1.76 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Franklin et al. 1966; Anicich 2003), respectively. While no literature reaction rate information has been found for reaction (19), a direct comparison of the estimated rates for reactions (19) and (17), obtained using the Su-Chesnavich capture rate model (Su & Chesnavich 1982; Tsikritea et al. 2022), indicates that the rates for the two reactions are very similar. For this reason, the literature reaction rate for reaction (17) of $k = 3.80 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ is assumed for reaction (19).

For the secondary product observed at m/z 54 (CH_3CNH^+), the only pathway requiring consideration is the one described by reaction (20) (Oldham 1999; Dechamps et al. 2007; Ascenzi et al. 2012), for which reported rate constants are in the range of $1.78\text{--}2.09 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Franklin et al. 1966; Vogt & Beauchamp 1975).

The corrected primary channel BRs for the reaction of He^+ with CH_3CN , measured as a function of the collision energy (E), are shown in Figure 3, while a comparison with BRs currently available in the astrochemical databases (McElroy et al. 2013; Wakelam et al. 2015) is shown in Figure 4. We note that the measured BRs are approximately constant over the studied collision energy range, spanning multiple orders of magnitude.

It is instructive to compare the BRs for CH_3CN ionisation measured by collision with He^+ ions with other astrochemically relevant ionising agents, namely electrons and photons. The dissociative electron ionisation of CH_3CN has been studied previously (Harland & McIntosh 1985; Parkes et al. 2019), with relative precursor-specific partial ionisation CSs having recently been reported (Parkes et al. 2019) for various fragment ions following dissociative single-electron ionisation at electron energies from 30 to 200 eV. The measured BRs were approximately independent of the electron energy used, with the primary product being that at m/z 40 (CH_2CN^+) with a BR of 0.42 at an electron energy of 40 eV. The next most significant channels were those at m/z 39 ($\text{HCCN}^+/\text{CCNH}^+$), 38 (C_2N^+), and 14 (CH_2^+), with respective BRs of 0.17, ~ 0.1 , and ~ 0.1 at the same electron energy of 40 eV.

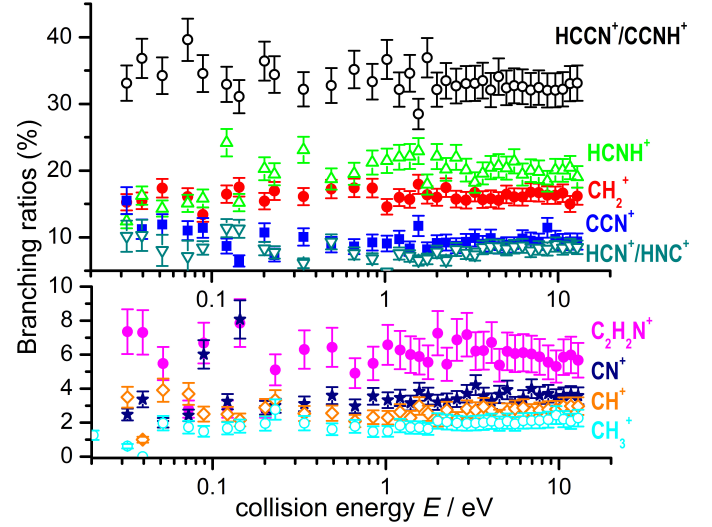


Fig. 3. Experimental BRs for the reaction of He^+ with CH_3CN as a function of collision energy.

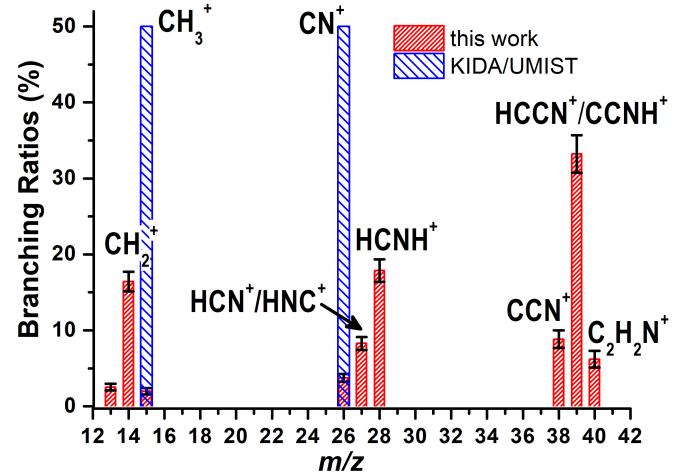


Fig. 4. Branching ratios (BRs) for the reaction between He^+ and CH_3CN as obtained in the present experiments (red bars) and in literature databases (McElroy et al. 2013; Wakelam et al. 2015) (blue bars).

Overall, the combined BR for the m/z 38, 39, and 40 products, that is, those where the C-C-N spine remains intact and equal to ~ 0.7 , is higher than the ~ 0.5 value obtained in the current work. This is indicative of a ‘softer’ ionisation, where H- and H_2 -ejection processes dominate. By contrast, while such processes are still significant in the case of the He^+ plus CH_3CN reaction, we observe a higher contribution from processes involving C-C or C-N bond cleavage. This difference is expected to arise from the differing nature of the ionisation processes involved, which in the present case lead to the generation of a highly electronically excited state of the CH_3CN radical cation, with further consideration given in Section 4.3.

The ionisation, isomerisation, and dissociation of methyl cyanide upon photon absorption in the gas phase have been extensively investigated (Turner 1970; Åsbrink et al. 1980; Holland et al. 1984; Gochel-Dupuis et al. 1992; Holland & Karlsson 2006; Huang et al. 2007; Schwell et al. 2008; Kukka et al. 2009; Polasek et al. 2016; Boran et al. 2017; McDonnell et al. 2020). Relative and/or absolute photoionisation CSs for the formation of both molecular and fragment ions have been measured in the vacuum ultraviolet (VUV) region from the ionisation

threshold at 12.20 eV up to higher energies where inner-shell photoionisation events are possible. Additionally, Ribeiro et al. (2015) reported electron-stimulated non-thermal ion desorption from acetonitrile ice upon bombardment with high-energy electrons (in the range 1000–2300 eV).

The most relevant study with which to compare the results of the present work is that of Kukka et al. (2009). These authors investigated the dissociation of acetonitrile following resonant core excitations by recording fragment ion mass spectra in coincidence with the resonant Auger electrons emitted in the decay process of the core-excited states using the photoelectron–photoion coincidence (PEPICO) technique. This technique allows the investigation of molecular fragmentation of specific ionic states generated by participator and spectator Auger decays. Interestingly, in the spectra recorded in coincidence with electrons having a binding energy of above ~22–23 eV (similar to the IE of He), the CH_3CN^+ parent cation is almost entirely absent from the ion mass spectrum. Correspondingly, the observed fragments are dominated by CH_n^+ (with $n = 1\text{--}3$), CNH_n^+ (with $n = 0\text{--}2$) and H_nCCN^+ (with $n = 0\text{--}2$), and the fragmentation pattern bears a close resemblance to that which we observe for collisions with He^+ . Furthermore, Kukka et al. (2009) show that the $\text{CH}_3^+/\text{CH}_2^+$ ratio is highly sensitive to the initial molecular ionic state, with the low ratio observed in our work (~0.12) being consistent with electron binding energies in the 24–27 eV range.

A previous combined experimental and theoretical study explored the isomerisation and dissociation pathways accessible following laser photoionisation of methyl cyanide (McDonnell et al. 2020). At the B3LYP/6-31++G(d,p) level of theory, pathways corresponding to reactions (7)–(13) were identified and, as also established elsewhere (Huang et al. 2007; Polasek et al. 2016), isomerisation through H migration leads to the stable linear (CH_2CNH^+) and cyclic (c-CHCHNH^+) isomers, both of which have distinctive fragmentation pathways. For instance, dissociation into CH_2^+ plus HNC is energetically favoured from the CH_2CNH^+ isomer, while H_2 ejection from CH_3CN^+ to give HCCN^+ is energetically preferred to the equivalent ejection from CH_2CNH^+ to yield CCNH^+ .

4.2. Experimental results: CSs as a function of collision energy and comparisons with capture models

Prior to performing the reaction dynamic treatment, we present a comparison between the experimental total CS trend as a function of the collision energy and those predicted by traditional capture models. Total CSs have been compared with those from capture models (Tsikritea et al. 2022) using the region with intermediate E values (between 1 and 2 eV) for normalisation, with results shown in Figure 5.

Notably, the Langevin model describing the interaction between a point-charge ion and a polarisable but non-polar neutral (black solid line in Figure 5) is not expected to reproduce the probability of capture between an ion and a polar molecule. In order to provide a more realistic model, the average dipole orientation (ADO) theory developed by Bowers and coworkers (Bass et al. 1975; Su et al. 1978) additionally considers the ion-permanent dipole interaction. To account for the average orientation of the dipole of the neutral species with respect to the ion, a scaling parameter ($c = \cos\theta$) is introduced. The parameter, with values ranging from 0 to 1, depends on the dipole moment and on the polarisability of the neutral. Using the parametrisation reported in Bass et al. (1975), a c value of 0.253 is used for the present system (blue short dashed line). The so-called

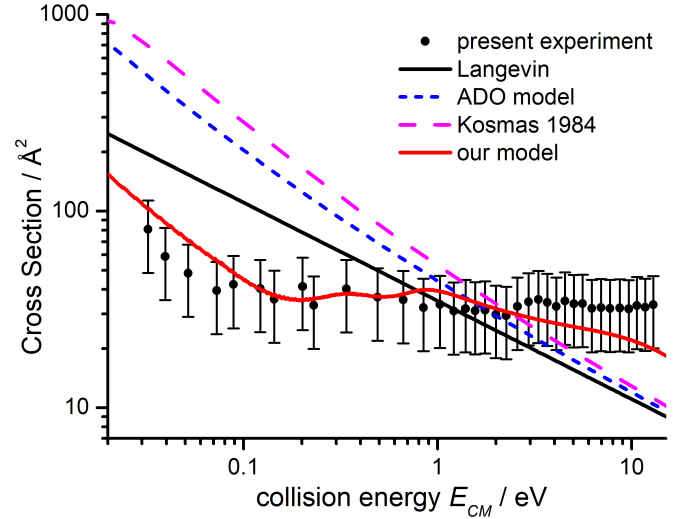


Fig. 5. Total CSs for the electron exchange reaction of He^+ with CH_3CN as a function of collision energy (E). The black filled circles are the total relative CSs, rescaled as detailed in the text. The lines represent total CSs as estimated from the following capture models: Langevin (black solid line), averaged dipole orientation (ADO) (blue short dashed line) (Bass et al. 1975; Su et al. 1978; Tsikritea et al. 2022) and the average $\cos\theta$ approach (Kosmas 1984) (magenta dashed line). The solid red line represents the computed CSs according to the theoretical treatment, based on an improved Landau-Zener-Stückelberg approach, and detailed in Sections 3 and 4.4. Error bars on the total relative CSs are $\pm 40\%$.

average $\cos\theta$ method proposed by Kosmas (1984) is similar to the ADO theory but gives expressions for the CSs as a function of both the relative kinetic energy of the colliding partners and the rotational energy of the polar molecule. The magenta dashed line is calculated using this model adapted to our experimental configuration, where the CH_3CN is in a collision cell at a fixed T . We therefore assume an average rotation energy equal to 0.039 eV, that is, $3/2kT$ with $T=305$ K (due to RF heating inside the octupole ion guide).

In all cases, the calculated CSs exhibit a sharp decrease with increasing E , in contrast to the experimentally observed trend. Such inconsistencies between predictions and experimental findings highlight the inadequacy of capture models for treating the charge-exchange process between He^+ and CH_3CN in the explored collision energy range.

4.3. Crossing points between entrance and exit channels

The collision energy (spanning a range from ~0.03 to ~10 eV in the present experiment) promotes non-adiabatic transitions at the crossings between the entrance and exit channels that are located in a wide range of separation distances. Moreover, the large difference in the IE of the two species ($\text{IE}(\text{He}) = 24.588$ eV = $\text{EA}(\text{He}^+)$ and $\text{IE}(\text{CH}_3\text{CN}) = 12.20 \pm 0.01$ eV (Linstrom & Mallard 2024; Holland et al. 1984; Gochel-Dupuis et al. 1992; Holland & Karlsson 2006)) does not permit crossings between entrance and exit channels in the case of an electron ejected by either the $2e(\pi_{\text{CN}})$ highest occupied molecular orbital (HOMO) of CH_3CN (see Figure 6 in Mancini et al. (2024)) or other outer valence molecular orbitals with binding energies of up to ~17 eV.

In order to have effective crossings between entrance and exit PE curves, the electron must be removed from a molecular orbital in the inner valence region, that is, with a binding energy

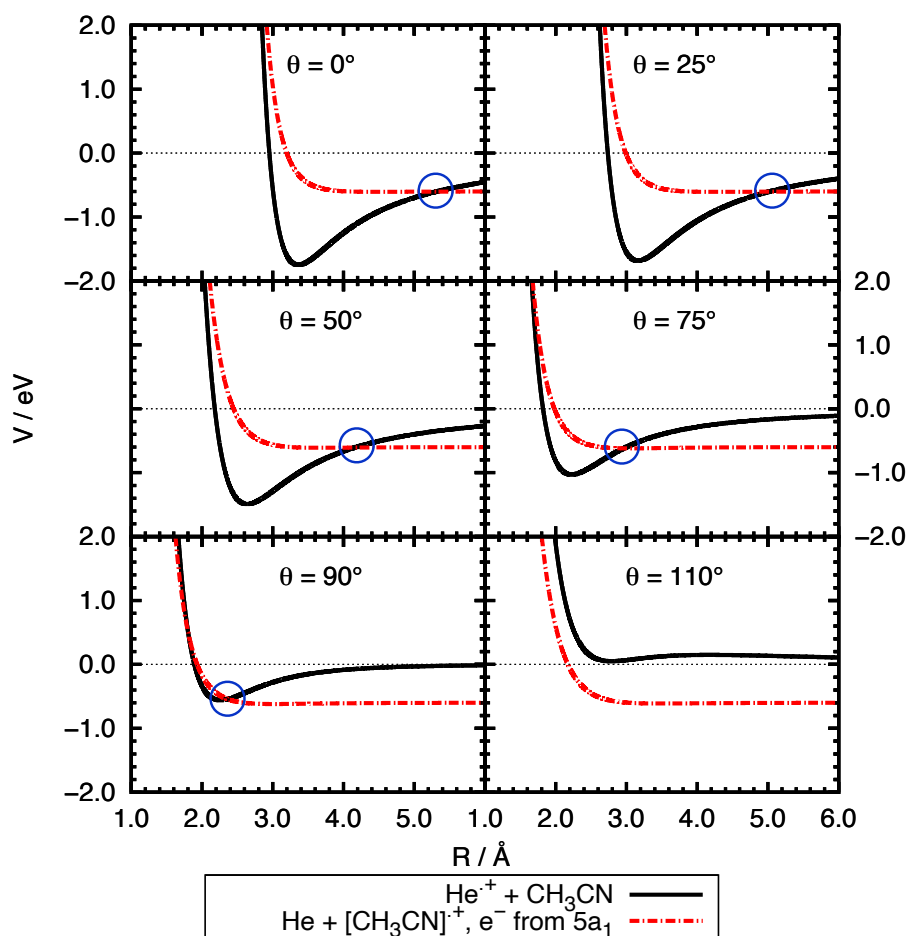


Fig. 6. PES crossings: PE curves of the entrance He^+ plus CH_3CN (solid black lines) and exit He plus $\text{CH}_3\text{CN}^{+*}$ (dotted-dashed red lines) channels for six different geometries determined by θ values equal to 0° , 25° , 50° , 75° , 90° and 110° . The red dotted-dashed lines have been calculated assuming the removal of an electron from the inner valence orbital $5a_1$ of CH_3CN , thus forming the radical cation in an electronically excited state, but that such removal does not substantially change the geometry of the ion with respect to the neutral molecule. The positions of crossings are highlighted with blue circles.

much higher than 12.20 eV. Photoelectron spectra (Åsbrink et al. 1980; Holland & Karlsson 2006) and electronic structure calculations (Mancini et al. 2024) suggest that the inner valence molecular orbital $5a_1$, responsible for the broad peak observed in the photoelectron spectrum in the region of 23–27 eV (see (Åsbrink et al. 1980) and Fig. 1 of Holland & Karlsson (2006)), has the most comparable energy to the IE of He, and is therefore the MO involved in the electron exchange process. Assuming the IE of $5a_1$ as the proper asymptotic level for the exit channels, a sequence of crossings is obtained where non-adiabatic charge-transfer effects are essential in order to trigger the ion-molecule reaction, as detailed in Mancini et al. (2024).

Figure 6 reports the curves obtained by PES cuts at six different geometries, corresponding to six different θ values from 0° to 110° . For each configuration, the solid black lines refer to the entrance channels (He^+ plus CH_3CN), while the dotted-dashed red lines are the scaled exit potentials (He plus $\text{CH}_3\text{CN}^{+*}$) resulting from the removal of an electron from the $5a_1$ orbital of CH_3CN . The zero of the energy scale is taken to coincide with the value at $R \rightarrow \infty$ of the PE cut of the entrance channel. The red dotted-dashed lines have been calculated assuming that the removal of an electron from an inner valence orbital does not substantially change the geometry of the radical cation with respect to the neutral molecule. We also note that the most

effective crossing points appear for θ varying from 0° up to $\sim 90^\circ$, while no crossings occur for θ significantly larger than 90° .

It is relevant to note that, in the proposed PES, predicted interactions for three reference configurations (i.e. $\theta = 0^\circ$, 90° and 180°) of the system in the exit channel, excluding the ion-induced dipole induction contribution (defined as V_{ind} in Mancini et al. (2024)), are in agreement – regarding binding energies to within $\sim 10\%$ and regarding the equilibrium distances to within 2–3% – with a full ab initio treatment of the neutral complex $\text{He}-\text{CH}_3\text{CN}$, as reported in Ben Khalifa et al. (2022).

4.4. Reaction dynamics treatment: Cross-section calculations

Our analysis of the experimental data was performed by adopting three different dynamical regimes of collision events. Since the PES driving the approach in the entrance channels is strongly anisotropic, exhibiting energy barriers that already exceed the average rotational energy of CH_3CN evaluated at room temperature at a separation distance of 20 Å, the reagents undergo natural orientation effects induced by the strong electric field gradient associated with the anisotropic interaction.

As a consequence, the collision complexes formed by the He^+ ion and the CH_3CN polar molecule tend to re-orient themselves in angular cones (*cone_i*) confined within the attractive part

of the PES, with the aperture of the acceptance cone changing with the collision energy E . In particular, considering the anisotropy of the potential well depths shown in Figure 6, we assume here that at low collision energies ($E \leq 0.1$ eV) most of the molecules are confined to a restricted angular cone ($cone_0$) that exhibits a maximum opening angle of $\theta = 25^\circ$. The opening angle increases up to $\theta = 45^\circ$ ($cone_1$) for energies in the range $0.3 \leq E \leq 0.6$ eV and again up to $\theta = 90^\circ$ for $E \geq 1.0$ eV ($cone_2$). The three angular cones are depicted in the bottom panel of Figure 2.

The total charge exchange CS $\sigma_T(E)$ is then calculated as a sum of the contributions from the different angular cones, with relative weightings depending on the E values. Accordingly,

$$\sigma_T(E) = [\sigma_{cone_0}(E) \cdot f_0(E) + \sigma_{cone_1}(E) \cdot (1 - f_0(E))] \cdot f_1(E) + \sigma_{cone_2}(E) \cdot (1 - f_1(E)), \quad (21)$$

where $f_i(E)$ is a Fermi weight function:

$$f_i(E) = \frac{1}{1 + e^{\frac{E - E_i}{E_{ti}}}}. \quad (22)$$

As in previous studies (Richardson et al. 2022), here the Fermi function has been exploited to define the transition from different dynamical regimes. The values of the parameters E_i and E_{ti} define the collision energy at which the two combined regimes of collision dynamics exhibit equal weightings and the rate at which the transition between the two calculation methods occurs, respectively. Here, E_0 , E_1 , E_{t0} , and E_{t1} have been selected to reproduce the experimental data via a trial-and-error analysis. Accordingly, for E_0 and E_1 we obtain the values 0.25 ± 0.02 and 0.65 ± 0.05 eV, respectively. For E_{t0} and E_{t1} we obtain 0.07 ± 0.01 and 0.13 ± 0.02 eV, respectively.

At low E , reactivity is predominantly the result of collision events governed by the strongest long-range attractions and primarily confined within $cone_0$. This leads to a significant attenuation of the reactivity, as all relevant crossing points between entrance and exit channels occur at large R_i . Furthermore, the non-adiabatic coupling $H_i(R_i, \theta)$ is weak due to the limited overlap between the atomic and molecular orbitals involved in the electron exchange process.

With increasing E , the reaction cone ($cone_1$) expands, and the crossing points shift to smaller R_i values, where the strength of $H_i(R_i, \theta)$ increases. At even higher E , the reaction cone further expands ($cone_2$), and the collision complexes can probe the entire semi-sphere of relative configurations where the PES is non-repulsive, that is, the region where the complete sequence of accessible crossing points occurs. Under such conditions, reactivity is influenced by the entire spectrum of crossing points and a plot of the crossing points as a function of θ is shown in Figure 7. While crossings at θ angles close to 90° are associated with small R_i and significant $H_i(R_i, \theta)$, the contribution from these crossings is attenuated by the increased values of E_i and, by extension, of the centrifugal potential, which limits the angular momentum l values that allow approach to R_i . Moreover, the PES cuts shown in Figure 6 suggest that, for some θ values, additional crossings beyond those considered in the present analysis are likely open. However, their contribution is expected to be negligible, because they occur in the repulsive region of the PES, and at short R_i values, where the limitations due to the centrifugal contribution are greatest.

Experimental and computed total CSs $\sigma_T(E)$ are compared in Figure 5, where the results from our model are shown in solid

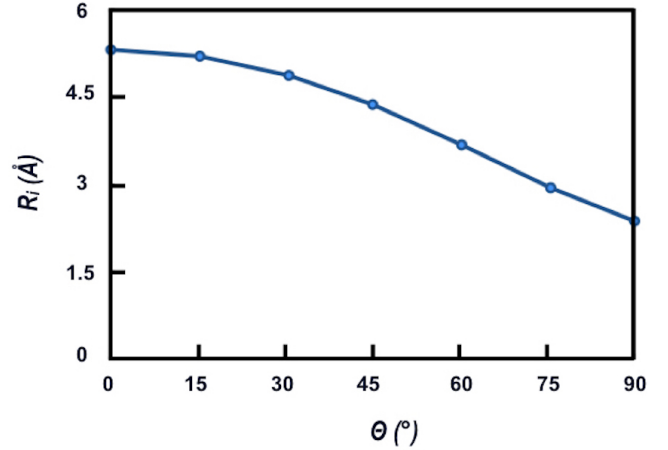


Fig. 7. Positions of crossings R_i in the entrance channel as a function of the angle θ .

red line. We note a good agreement in terms of the energy dependence of the measured CS in a wide range of E values. According to our treatment, the barriers in the entrance PES tend to channel most of the collision complexes in the semi-sphere of the relative orientations, where the attraction dominates and the size of the CH_3 group, mostly responsible for the short-range repulsion, plays a minor role. However, the effectiveness of the orientation tends to diminish at very high E values.

At low collision energies, the CSs evaluated using capture models (see black solid, blue short dashed, and magenta dashed lines in Figure 5) are higher than those calculated here due to the fact that they do not consider the features of the crossing points and due to the selective role of the centrifugal barriers emerging in the entrance channels. At high collision energies, that is, when the probed intermolecular distances decrease, our treatment gives CSs that converge to those of the capture model, although the latter do not take into account the size of the CH_3 group, as the interaction anisotropy is evaluated considering only the ion-permanent dipole interaction component.

4.5. Rate constants and astrochemical relevance

From the CSs obtained using the approach described above, it is possible to estimate the reaction rate coefficients as a function of temperature $k(T)$ by averaging the computed total CSs over a Maxwell-Boltzmann distribution of collision energies, as detailed in Ascenzi et al. (2019). Results are presented in Figure 8 with a solid red line, where they are compared with values from various astrochemical databases and a range of capture models.

The rate obtained using the pure Langevin model (i.e. omitting the ion – permanent dipole interaction) is given by the solid black line, while the cyan line is from the KIDA database (Wakelam et al. 2015), which uses the expression from the Su and Chesnavich model derived from an empirical fit of variational transition state theory and classical trajectory calculations for point charged ions and polar neutrals (Su & Chesnavich 1982). The blue line with triangles is from the UMIST database (Millar et al. 2024), which proposes an expression for $k(T)$ assuming a value of k at $T=300$ K equal to $1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, taken from Prasad & Huntress (1980). The dashed blue line is from the scaled averaged dipole orientation (ADO) model and successive variants (already discussed in Sect. 4.2), with a c value of 0.253. It should be noted that this c value refers to an average orientation calculated at 300 K by Bass et al. (1975) and

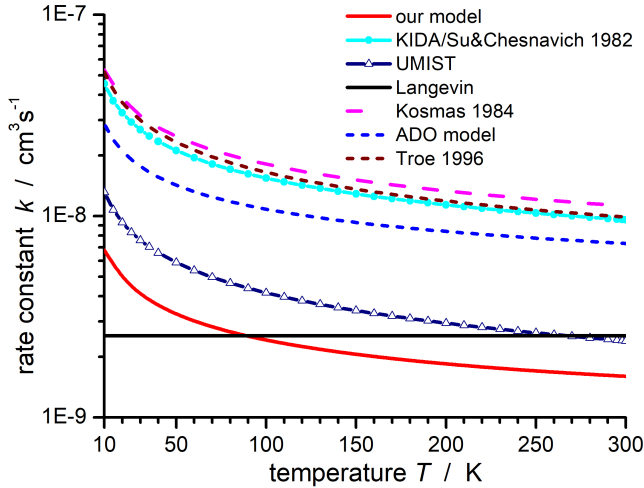


Fig. 8. Total rate constants k as a function of temperature T for the reaction of He^+ with CH_3CN . Solid red line: our model, solid black line: Langevin model, cyan line with dots: KIDA database (Wakelam et al. 2015; Su & Chesnavich 1982), blue line with triangles: UMIST database (Millar et al. 2024), dashed blue line: scaled averaged dipole orientation (ADO) with $c = \overline{\cos\theta} = 0.253$ (Bass et al. 1975; Su et al. 1978), dashed magenta line: average $\cos\theta$ method (Kosmas 1984), dashed brown line: statistical adiabatic channel model (SACM), Eq. (5.2) from Troe (1996).

Su et al. (1978). The dashed magenta line is from the average $\cos\theta$ method (Kosmas 1984) and the dashed brown line corresponds to an analytical expression for the rate constant derived from the statistical adiabatic channel model (SACM) developed by Troe (1996, see their Eq. (5.2)).

Interestingly, in a recent experiment, the translational temperature dependence of the reaction rate constant for the charge-exchange process between Ne^+ ions and CH_3CN was measured at low temperatures (Okada et al. 2020), with the smaller measured reaction probability with respect to typical ion-polar molecule reactions at temperatures above 5 K being consistent with the $k(T)$ values obtained with our model for the case of He^+ ions.

Previous astrochemical models, which used the reactions rates from the KIDA database, suggested that the CH_3CN observed in discs is mostly formed on grains, as gas-phase chemistry cannot account for the large observed abundances (Öberg et al. 2015; Loomis et al. 2018). These studies argued that, if N-bearing molecules are mostly formed on grains and therefore reflect the ice composition, the abundance ratios of CH_3CN and smaller N-bearing compounds (namely HCN , HC_3N) in discs can be compared with those in comets to test whether planets and small bodies inherit (at least partially) their composition from the disc where they are formed. Our study, however, indicates that the rate coefficient for the destruction of CH_3CN through collisions with He^+ evaluated at 10 K might be as low as $\sim 6.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a rate that is almost one order of magnitude lower than that currently reported in KIDA (Wakelam et al. 2015). Combined with the revised chemical network for formation of CH_3CN (Giani et al. 2023), this suggests that, in contrast with what has previously been proposed, methyl cyanide in discs could be mostly the product of gas-phase processes. The formation of abundant CH_3CN in the gas phase would explain the routine detection of CH_3CN in planet-forming discs out to large radii (a few hundred au), that is, beyond the CH_3CN snowline, where ices cannot be thermally evaporated (see Ceccarelli et al. (2023)

and references therein for the binding energy of CH_3CN). This is in contrast with CH_3OH , which is only formed on grain surfaces at low temperatures via CO freeze-out and subsequent hydrogenation reactions (Watanabe & Kouchi 2002), and so is expected to be detected only where grains are sublimated, inside the CH_3OH snowline. Moreover, CH_3OH is only detected in a few discs, such as in transition discs with an inner cavity (Booth et al. 2021; Booth et al. 2023), or in outbursting discs (Lee et al. 2019), where the snowline is pushed outwards. The low amount of methyl cyanide measured in comets compared to the larger values found for methanol (0.008–0.054% vs 0.7 to 6.1 % with respect to water (Biver & Bockele-Morvan 2019) may further support this hypothesis. Our findings are therefore expected to have important implications for the origin of methyl cyanide in planet-forming discs, as well as for the comparison of the abundance ratios of N-bearing molecules in discs and in comets.

5. Conclusions

We used guided ion beam experiments to determine the collision energy dependence of total (σ_T) and partial CSs as well as BRs for the reaction of He^+ with CH_3CN . While we varied the collision energy, E , by about three orders of magnitude (from thermal up to hyper-thermal conditions), $\sigma_T(E)$ remained approximately constant (changing by only a factor two).

These experimental findings contrast with predictions from widely used capture models. In particular, the $\sigma_T(E)$ values predicted by capture models exhibit a sharper decrease with increasing E than is observed experimentally. This is attributed to the fact that such models do not take into account the basic features of the crossing points between entrance and exit channels, which occur at much shorter distances than the maximum of the centrifugal barrier, and where non-adiabatic effects are triggered. Therefore, the possibility of reaching such crossings in the entrance channel, combined with the selective influence of their features and the centrifugal barrier, strongly limits the values and effectiveness of the orbital angular momentum, l , in promoting the reaction. At high E , the probed intermolecular distances decrease and our treatment and the capture models tend to converge. This is because capture models do not consider the features of the crossings controlled by the interaction anisotropy, as they only evaluate the ion-permanent dipole interaction component. However, this omission is largely offset by the fact that they also do not account for the influence of the size of the CH_3 group.

To rationalise the experimental findings, we formulated detailed PESs for the entrance and exit channels of the reaction. The PES in the entrance channel exhibits a high degree of anisotropy, as the interaction is strongly modulated by the molecular orientation with respect to He^+ . During the collisions, the CH_3CN rotational motion perpendicular to its C_{3v} symmetry axis, evaluated under thermal conditions typical of ion-guided experiments, is hindered by comparatively high interaction potential energy barriers. In particular, at $R = 20 \text{ Å}$, the ratio between the effective barrier height and the average rotational energy amounts to a factor 2, increasing up to a factor of ~ 35 at $R = 5 \text{ Å}$ and even higher for lower R . The polar CH_3CN molecule therefore adopts a “natural” orientation in the electric field gradient associated with the strong anisotropic interaction potential. The orientation effect is expected to increase with decreasing E , becoming more effective than that observed in less anisotropic systems (Gisler & Nesbitt 2012; Li et al. 2014; Falcinelli et al. 2023; Cappelletti et al. 2024; Ploenes et al. 2024).

Therefore, the present investigation casts light on important stereo-dynamical effects whose role becomes prominent under thermal and subthermal conditions. In particular, with decreasing E the polar CH_3CN molecule tends to be channeled into restricted angular cones confined around $\theta = 0^\circ$, where the PES has the maximum attraction. However, under such conditions, the effective crossings between entrance and exit channels manifest at larger R values, where the reduced overlap between orbitals involved in the electron transfer strongly limits the reactivity. Our treatment provides rate coefficients expected to be reliable, within a factor 2–3, down to cold conditions ($T \sim 10$ K), where our results represent a lower limit on the true values. The main uncertainty arises from neglecting – in the semiclassical calculation of CSs – quantum effects (tunnelling through the centrifugal barrier), whose role strongly increases with decreasing T .

Our results for the reaction rates appear to be significantly different from those currently adopted in astrochemical network databases. Based on the findings presented and discussed here, we propose that methyl cyanide in protoplanetary discs could be mostly the product of gas-phase processes. In conclusion, it should be stressed that a complete characterisation of the chemical reactions – and their rates – leading to the formation and destruction of CH_3CN is crucial in order to update the astrochemical networks and for the meaningful comparison of the chemical composition of discs and comets.

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