The reactivity of methanimine radical cation (H_2CNH^+) and its isomer aminomethylene (HCNH_2^+) with methane

V. Richardson, Christian Alcaraz, W.D. Geppert, M. Polásek, C. Romanzin, D. Sundelin, R. Thissen, P. Tosi, J. Žabka, D. Ascenzi

► To cite this version:

V. Richardson, Christian Alcaraz, W.D. Geppert, M. Polásek, C. Romanzin, et al.. The reactivity of methanimine radical cation (H_2CNH^+) and its isomer aminomethylene (HCNH_2^+) with methane. Chemical Physics Letters, 2021, 775, pp.138611. 10.1016/j.cplett.2021.138611 . hal-03280632

HAL Id: hal-03280632

<https://hal.science/hal-03280632>

Submitted on 7 Jul 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The reactivity of methanimine radical cation ($\text{H}_2\text{CNH}^{+\bullet}$) and its isomer aminomethylene ($\text{HCNH}_2^{+\bullet}$) with methane

V. Richardson^a, C. Alcaraz^{b,c}, W. D. Geppert^d, M. Polášek^e, C. Romanzin^{b,c}, D. Sundelin^d, R. Thissen^{b,c}, P. Tosi^a, J. Žabka^e and D. Ascenzi^{a,*}

^a Department of Physics, University of Trento, Via Sommarive 14 – 38123 Italy

^b Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France

^c Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Saint Aubin, Gif-sur-Yvette, France

^d Department of Physics, Stockholm University, Roslagstullsbacken 21, 10691 Stockholm, Sweden

^e J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, Prague 8, 18223 Czech Republic

* corresponding author: e-mail daniela.ascenzi@unitn.it phone: +39 0461 281693

Abstract

Experimental and theoretical studies are presented on the reactions of the isomeric radical cations $\text{H}_2\text{CNH}^{+\bullet}$ and $\text{HCNH}_2^{+\bullet}$ with CH_4 . Ionic isomers were generated selectively by VUV dissociative photoionization of azetidine and cyclopropylamine precursors respectively. Both exclusively give H_2CNH_2^+ plus CH_3^+ as products, but differences are observed related to a competition between stripping and complex-mediated H-transfer. Astrochemical implications for Titan's atmosphere are briefly discussed, where the presence of methanimine (H_2CNH), a key prebiotic molecule and a potential precursor for tholins, is proposed on the basis of atmospheric models and the observation of CH_2NH_2^+ ions in Cassini mass spectrometric data.

Keywords: interstellar medium; rate constants; ion-molecule reactions; astrochemistry; molecular astrophysics; Titan's atmosphere; methane activation; isomer; methanimine; aminomethylene

1. Introduction

The reactivity of methane with a range of ions has been the focus of several experimental and theoretical studies [Schroder1995; Ryan1995; Bohme2009] due to its relevance to a variety of environments and to the interest in the activation of C-H bonds in saturated species. The activation of methane has been studied via reaction with cations and radicals [dePretis2009, Dietl2013, Schwarz2015, Schwarz2017, Viggiano2020] with two mechanisms being proposed: direct hydrogen transfer and reaction via intermediate complexes.

Here, we focus on the reaction of CH_4 with the two lowest energy isomers of $[\text{CH}_3\text{N}]^{+\bullet}$: $\text{H}_2\text{CNH}^{+\bullet}$ and $\text{HCNH}_2^{+\bullet}$. Though they both contain a radical moiety and a cationic nitrogen, $\text{H}_2\text{CNH}^{+\bullet}$ has a radical cation character while the $\text{HCNH}_2^{+\bullet}$ isomer is distonic, thus allowing for a comparison of the chemistry of the two functionalities independently, as well as in combination. Additionally, these are the two simplest imine cations, and so their reactions should provide insight into the reactivity of this functional group, which has been identified as a potential core building block in the formation of amino acids [Aponte and Elsila 2017].

From an astrochemical perspective the title reaction is relevant to the chemistry of methanimine $\text{H}_2\text{C}=\text{NH}$ and its related ions in Titan's atmosphere. Here, the presence of considerable amounts

of neutral methanimine has been proposed by models [Vuitton2019, Lavvas2008] on the basis of an intense peak at m/z 30 present in the mass spectrum from the Ion Neutral Mass Spectrometer of Cassini and attributed to protonated methanimine CH_2NH_2^+ [Vuitton2006, Vuitton2007, Balucani19].

Such models have predicted only a minor presence of $\text{H}_2\text{CNH}^{++}/\text{HCNH}_2^{++}$ in Titan's atmosphere ($1.1 \times 10^{-2} \text{ cm}^{-3}$ [Vuitton2007]) though this could be due to their high reactivity and, consequently, fast destruction. A theoretical study [Skouteris2015] has indicated that the barriers for bond-forming reactions starting from neutral methanimine are unfeasibly high for the low temperature environments of Titan, but the formation of covalently bound adducts from the ionic form is in many cases barrierless.

The idea has therefore been put forward that methanimine radical cations might be the basis for methanimine polymerization [Skouteris2015], eventually leading to the build up to detected complex ions [Westlake2014, Vuitton2019]. These, in turn, may account for the formation of the Titan nitrogen-rich aerosols. Since $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} are stable species separated by a high isomerization barrier [Nguyen1994], the reactivity of both isomers should be addressed, as well as the possibility for their isomerization. As CH_4 is the most abundant hydrocarbon in Titan's atmosphere, it is a logical starting point for reactivity studies.

In this paper we describe an experimental method to selectively produce the title ions by dissociative photoionization of cyclopropylamine and azetidine using tuneable VUV synchrotron radiation. In **Sec. 3** experimental and theoretical results on the dissociative photoionization of the precursors are presented and potential contaminations by isobaric ions are discussed. In **Sec. 4** results from the reactions of $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} cation isomers with CH_4 are presented, together with computational data to help rationalise the observations. In the accompanying paper [Sundelin21] the reactivity with C_2H_4 is presented.

2. Experimental and computational Sections

2.1 Experimental set-up

Experiments were performed using the CERISES apparatus [Alcaraz 2004; Cunha 2015] at the DESIRS beamline [Nahon2012] of the SOLEIL synchrotron radiation facility. CERISES is a guided ion beam tandem mass spectrometer composed of two octopoles located between two quadrupole mass filters that permits investigation of bi-molecular reactions of mass-selected ions. By measuring the yields of parent- and product-ions, absolute cross sections (CS) are derived as a function of both photon and collision energy.

$[\text{CH}_3\text{N}]^{++}$ isomers were produced by dissociative photoionization of suitable gaseous precursors (see **Section 3**) introduced at roughly 10^{-6} mbar in the ion source. CH_4 was introduced in the reaction cell at a dynamic pressure of 2×10^{-7} bar, which guarantees operation close to a single collision regime, reduces secondary reactions and limits the parent ion attenuation to less than 10%. The absolute pressure was measured using the MKS 398H differential manometer.

The photon energies (E_{phot}) used to generate $[\text{CH}_3\text{N}]^{++}$ ions are in the range of 9.5–14 eV. Monochromator slits were set to define photon energy resolution of 20 to 40 meV. The gas filter [Mercier 2000] of the beamline used Argon to remove photons above 15.7 eV. The absolute scale of the photon energy was based on absorption lines of Argon around 11.828 and 14.304 eV [Minnhagen 1973, NIST ASD], with systematic shifts of about 10–20 meV above their tabulated values.

The mass filter resolution was adjusted in order to maximize signal and provide sufficient removal of ions at adjacent mass units. A pollution of ~0.01% of neighbouring ions for Q1 and ~0.1% for Q2 is estimated at the lowest collision energy, which for the later increases to 1.2% at an acceleration potential of 20 V. Collision energy was set by the difference between the ion source and the reaction cell potentials. This was determined by the retarding potential method [Teloy 1974], giving a parent beam FWHM of 0.4 eV in the LAB frame. By changing the potentials of the reaction cell and all subsequent elements up to 20V, the collision energy can be spanned from ~0.06 eV up to ~10 eV in the centre-of-mass frame (E_{CM}).

Acquisitions, both for photon and collision energy scans, were performed by counting signal for all ionic species at a single point before moving to the next one. This drastically reduces effects of pressure drifts in source and reaction cell.

2.2 Theoretical Methodology

Relevant structures in the PES describing the dissociative ionisation of the cyclopropylamine and azetidine precursors were performed using Wavefunction's Spartan '18 suite [Spartan]. For stable structures, corresponding to energy minima, calculations were conducted at the G3 level, which is a combination of Hartree-Fock and wave function-based electron correlation methods, with the output being the enthalpy of formation at 298 K. For transition states, calculations were conducted at the ω B97X-D/cc-pVTZ level. ω B97X-D is a Range Separated Hybrid Generalized Gradient Approximation functional, which uses Grimme corrections (-D) in order to account for dispersive interactions. Cc-pVTZ refers to the Correlation consistent polarized Valence Triple Zeta basis set, which is a triple-zeta basis set intended specifically for use in correlated calculations.

Calculations of the reaction mechanisms of $\text{HCNH}_2^{++}/\text{H}_2\text{CNH}^{++}$ plus CH_4 were performed using GAUSSIAN [GAUSSIAN]. Intermediate structures, *i.e.* minima and transition states, were calculated at the MP2/6-31G*, MP2/6-311++G** and MP2/cc-pVTZ levels. The identity of transition states and minima were checked by frequency calculations and zero-point energy corrections were employed to the obtained energies. IRC calculations were performed at the MP2/6-31G* level to ensure that the transition states connect the correct minima. Energy calculations were carried out for all stationary points at the CCSD(T)/6-311++G** and CCSD(T)/cc-pVTZ levels with zero-point energy corrections taken from the MP2/6-311++G** and MP2/cc-pVTZ levels respectively. Reactants and product geometries and energies were also calculated at the same level (including zero-point energy corrections) and their energies subtracted from the optimizations of the transition states and minima, resulting in the relative energies E_{rel} . Full results are given in the **Supplementary Information 1** (Tables 1-4 and Figs. 1-3).

3. Results and discussion: generation of different $[\text{CH}_3\text{N}]^{++}$ isomers

The HCNH_2^{++} and $\text{H}_2\text{CNH}^{++}$ isomers have been generated via dissociative photoionization of cyclopropylamine ($c\text{-C}_3\text{H}_5\text{NH}_2$) and azetidine ($c\text{-CH}_2\text{CH}_2\text{CH}_2\text{NH}$), respectively, as proposed in [Audier03, Polce97, Burgers84]:

(1b)

3.1 Dissociative photoionization of cyclopropylamine

The photoionization and subsequent H ejection from cyclopropylamine has been studied both experimentally and theoretically [Bouchoux1998, Bouchoux2000] where an ionization energy IE for $c\text{-C}_3\text{H}_5\text{NH}_2$ was given as 8.78 ± 0.03 eV. These authors demonstrated that the cyclic structure ring-opens upon ionization at threshold to give $\text{CH}_2\text{CH}_2\text{CHNH}_2^{++}$. In Fig. 1 calculations are presented on the energetics of the fragmentation pathways of this ion over the studied photon energy range. A comparison with literature data is given in Table S1 of the Supplementary Information 2.

The photoionization efficiency (PIE) curves (*i.e.* ion yields as a function of photon energy) for the dissociative ionization products of cyclopropylamine at m/z 29 (sum of HCNH_2^{++} and C_2H_5^+), m/z 28 (sum of HCNH^+ and C_2H_4^+) and m/z 30 (H_2CNH_2^+) are shown in Fig. 2, where the observed appearance energies (AEs) are reported. To evaluate the AEs the method of linear threshold extrapolations of the PIE curves is used [Chupka71, Traeger1981, Castrovilli2014].

However, the PIE curve at m/z 29 does not show any well-defined onset but rather a curved threshold region that could not be fitted with a linear regression. In this case the experimental AE is obtained from the actual onset of the PIE curve, taking the first point above noise level as a rough estimate. We refrain from transforming experimental AEs into reaction enthalpies/energies since it will require accounting for Franck Condon factors, the presence of excited states of the parent ion and the thermal enthalpy correction term. This is beyond the scope of the paper, which doesn't aim to measure the heat of formation of $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} ions but rather their reactivity. We also note that the AE of the parent ion (m/z 57) and the H loss channel (m/z 56) are at 8.7 ± 0.1 eV and 9.2 ± 0.1 eV respectively (data not shown), in agreement with previous studies [Bouchoux et al. 1998 ; Bouchoux et al. 2000].

Dissociative ionization to give HCNH_2^{++} plus C_2H_4 via the open structure $\text{CH}_2\text{CH}_2\text{CHNH}_2^{++}$ has a calculated reaction enthalpy of 10.41 eV, in agreement with the 10.42 ± 0.11 eV literature value [Nguyen1994]. Our experimental AE (corresponding to the first point above noise level, see inset a) in Fig. 2) of 10.2 ± 0.1 eV is lower than previous value of 11.00 ± 0.05 eV [Burgers1984] obtained via dissociative electron ionization with energy selected electrons. The identification of the fragment ion as the aminomethylene isomer has been previously proposed on the basis of collisionally activated dissociation, metastable ion mass spectra and charge reversal experiments [Polce97, Burgers84].

Production of HCNH^+ in combination with C_2H_5^+ may proceed via a [1, 4] H shift to the $\text{CH}_3\text{CH}_2\text{CHNH}^+$ intermediate structure. Our calculations give an overall reaction enthalpy of 10.22 eV, in agreement with the 10.30 ± 0.18 eV that can be estimated from values reported in [Holmes2006]. The experimental AE of 10.40 ± 0.26 eV for m/z 28 (see inset b) in Fig. 2) is consistent with the opening of this fragmentation channel, which has an AE close to the HCNH_2^{++} isomer. Given that the yield of m/z 28 fragment from cyclopropylamine is more intense than that

calculated enthalpy of 10.02 eV matches the literature value of 10.02 ± 0.14 [Holmes2006, NIST Chem] as does our experimental AE of 10.20 ± 0.05 eV.

In summary, dissociative photoionization of cyclopropylamine allows for the production of the HCNH_2^{++} isomer with $\text{AE} = 10.2 \pm 0.1$ eV and potential contamination from C_2H_5^+ limited to high photon energies ($E_{\text{phot}} > 11.4$ eV).

Fig. 2: PIE curves for the dissociative photoionization of cyclopropylamine to give ions at m/z 29 (red data), m/z 28 (blue data) and m/z 30 (black data). Insets **a)** **b)** and **c)** show zooms in the threshold region for the corresponding m/z values. Dashed lines are the linear extrapolations used to extract the experimental AEs, when possible.

3.2 Dissociative photoionization of azetidine

The production of $\text{H}_2\text{CNH}^{++}$ via a $[2 + 2]$ cycloreversion reaction of azetidine has been proposed previously [Burgers1984] where the AE for m/z 29 ions was measured via energy selected electrons to be 10.46 ± 0.05 eV. The identification of the charged fragment as $\text{H}_2\text{CNH}^{++}$ has been proposed on the basis of collisionally activated dissociation, metastable ion mass spectra and charge reversal experiments [Burgers1984, Polce1997]. A photoionization-mass spectrometry investigation of azetidine measured the AE for this channel as 10.32 ± 0.08 eV [Tarasenko 1986; Holmes1992] and for the formation of HCNH^+ as 9.98 ± 0.02 eV.

To the best of our knowledge the full dissociative ionization of azetidine has not been investigated experimentally or theoretically. A scheme of the most relevant dissociation pathways from calculations is presented in **Fig. 3** and a comparison with literature data is given in **Table S2** of the **Supplementary Information 2**. The PIE curves for the dissociative ionization products of azetidine at m/z 29 (sum of HCNH_2^{++} and C_2H_5^+) and m/z 28 (sum of HCNH^+ and $\text{C}_2\text{H}_4^{++}$) are presented in **Fig. 4**, where AEs are derived as discussed in the previous section. We note that

the AE of the m/z 57 parent ion (8.7 ± 0.1 eV) and the m/z 56 H loss channel (9.2 ± 0.1 eV), data not shown, are in agreement with previous work [Tarasenko 1986].

Fig. 3: Scheme of the most relevant dissociations pathways upon ionization of azetidine. Enthalpy differences (in eV, relative to the azetidine neutral) are calculated at the G3 level for the PES minima and at DFT level (ω B97X-D with cc-pVTZ basis set) for the transition states

Production of the target ion $\text{H}_2\text{CNH}^{++}$ in combination with C_2H_4 requires a rearrangement to the open structure $\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ from which dissociation proceeds barrierlessly with an overall calculated reaction enthalpy of 10.35 eV, in excellent agreement with the value 10.36 ± 0.16 eV [Nguyen1994]. Our experimental AE of 10.2 ± 0.1 eV (corresponding to the first point above noise level, see inset a) in Fig. 4) is consistent both with these calculations and with previous experimental values [Tarasenko 1986; Holmes1992].

Production of HCNH^+ in combination with C_2H_5^+ proceeds by a [1, 4] H shift from $\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ to yield $\text{CH}_3\text{CH}_2\text{NHCH}^{++}$. The latter fragments into products with a barrier of 10.14 eV. Our experimental AE for m/z 28 of 10.22 ± 0.06 eV is in fair agreement both with the computational value and the literature reaction enthalpy of 10.08 ± 0.22 eV [Holmes2006]. Similarly to the cyclopropylamine case, this fragmentation channel opens at similar E_{phot} as the $\text{H}_2\text{CNH}^{++}$ isomer.

The formation of C_2H_5^+ in combination with HCNH^+ is a more endothermic channel which proceeds via $\text{CH}_3\text{CH}_2\text{NHCH}^{++}$ with a calculated reaction enthalpy of 11.17 eV (in good agreement with the literature estimate of 11.13 ± 0.08 eV [Baer2000, ATcT]). The formation of C_2H_5^+ in combination with H_2CN^+ has a smaller reaction enthalpy (10.80 eV) but it is inhibited by a reaction barrier (TS located at 11.30 eV). Hence the production of C_2H_5^+ as a contaminant of the $\text{H}_2\text{CNH}^{++}$ isomer should be considered when working at photon energies above ~ 11 eV.

$\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ can also fragment to give $\text{C}_2\text{H}_4^{++}$ plus H_2CNH with a reaction enthalpy of 10.97 eV, in good agreement with the literature value of 10.95 ± 0.23 eV [NIST ChemWeb, Holmes1992, ATcT]. The formation of $\text{C}_2\text{H}_4^{++}$ from azetidine is therefore expected to have a lower AE than from cyclopropylamine. In the azetidine case, one should therefore consider the effect of isobaric impurities due to $^{13}\text{CCH}_4^{++}$ as well as $\text{H}^{13}\text{CNH}^+$ when mass selecting ions at m/z 29. However, since the yield of m/z 29 fragment from azetidine is more intense than that for m/z 28 with the exception of the threshold region (see Fig. 4), any contamination is expected to be minor.

Fig. 4 PIE curves for the dissociative photoionization of azetidine to give ions at m/z 29 (red data) and 28 (blue data). Insets **a**) and **b**) show zooms in the threshold region for the corresponding m/z values. Dashed line is the linear extrapolation used to extract the experimental AEs, when possible.

4. Results and discussion: reactivity experiment

To exclude any interference from isobaric contaminants arising from ^{13}C ($\text{H}^{13}\text{CNH}^+$ and $^{13}\text{CCH}_4^{++}$) at m/z 29, we have performed preliminary experiments with CH_4 selecting the m/z 28 ions (a combination of HCNH^+ and $\text{C}_2\text{H}_4^{++}$) from dissociative photo-ionization of cyclopropylamine and azetidine. We observe no reactivity (i.e. CS smaller than $0.02 \text{ \AA}^2$), in agreement with literature: both HCNH^+ and $\text{C}_2\text{H}_4^{++}$ are unreactive towards methane ($k < 1.00 \cdot 10^{-13}$ [Anicich 2003]). C_2H_5^+ is known to have a small reactivity with CH_4 ($k = 9 \cdot 10^{-14}$ [Anicich 2003]) leading to C_3H_7^+ (m/z 43) plus H_2 . However, no ion counts at m/z 43 are detected upon reaction of m/z 29 from both precursors, even at the photon energies at which C_2H_5^+ production is energetically possible.

Upon reaction with CH_4 both isomers show a unique product at m/z 30, which corresponds to H abstraction from methane to give CH_2NH_2^+ plus $\text{CH}_3\cdot$:

Only **2a** has been studied in the literature [Audier2003] (where no values of absolute rate constants or CS are given) and the main channel is H atom abstraction, in agreement with our results. Calculations as part of this study indicate that reactions (**2a**) and (**2b**) are exothermic by 0.64 and 0.83 eV respectively, in good agreement with literature values (see **Table S3** in the **Supplementary Information 2**).

The CS dependences on photon energy (see **Fig. 5**) are similar for both isomers. Data is noisy just above threshold due to low parent ion signals but it shows that CSs are approximately constant as a function of photon energy at both collision energies and for both isomers. Given the exothermicities of **2a** and **2b**, it should be expected that they show little dependence on the (here unknown) internal energy of the reactant ion, supporting this observation.

Fig. 5: Reactive CSs as a function of E_{phot} for the reaction of HCNH_2^{++} (top) and $\text{H}_2\text{CNH}^{++}$ (bottom) with CH_4 at fixed collision energies (E_{CM}) indicated in the figure. The vertical dashed lines show the photon energies at which spectra as a function of E_{CM} have been collected (see Fig. 6)

Fig. 6 shows the collision energy trends of the CSs probed at fixed $E_{\text{phot}} = 11.48$ eV (plus $E_{\text{phot}} = 11.98$ eV only for HCNH_2^{++}). For the HCNH_2^{++} isomer, apart from a contribution at $E_{\text{CM}} < 0.1$ eV, the CS increases with increasing E_{CM} (up to about 2 eV), with a plateau at higher E_{CM} . For $\text{H}_2\text{CNH}^{++}$ the CS is larger than for HCNH_2^{++} at low E_{CM} with a more gentle rise in the 0.2-2 eV range.

Fig. 6: Reactive CSs as a function of collision energy E_{CM} for the reaction of HCNH_2^{++} (top) and $\text{H}_2\text{CNH}^{++}$ (bottom) with CH_4 measured at fixed photon energies (E_{phot}). The dotted lines indicate the collision energies at which spectra have been taken as a function of E_{phot} (see Fig. 5).

Calculations have identified van der Waals adducts for the two reacting isomers through which reaction can proceed (see Fig. 7 for a sketch of the pathways). The reactant radical cations are both planar molecules with a doublet ground state. Previous calculations [Nguyen1994] at the RCCSD(T) level of theory give the electronic energy of $\text{H}_2\text{CNH}^{++}$ as 23–24 $\text{kJ}\cdot\text{mol}^{-1}$ higher than HCNH_2^{++} . This value reduces to 16 $\text{kJ}\cdot\text{mol}^{-1}$ when taking the vibrational zero-point energies and thermal corrections into account, at both 0 and 298 K. Our calculations give a difference of $\sim 18 \text{ kJ}\cdot\text{mol}^{-1}$ for the energies of the two isomers, in good agreement with previous results. In the following discussion energies are given (in $\text{kJ}\cdot\text{mol}^{-1}$).

For both isomers, the lowest energy complex is formed barrierlessly and corresponds to N-terminal approach of the ion to the neutral. For $\text{H}_2\text{CNH}^{++}$ this structure, **A1**, is 24.8 $\text{kJ}\cdot\text{mol}^{-1}$ below the energy of the reactants, while for HCNH_2^{++} the corresponding structure **A2** lies 18.2 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants. **A1** is able to transfer an H from the methane to the ion to give **A4** (which is common to both isomers and lies 107.2 $\text{kJ}\cdot\text{mol}^{-1}$ below $\text{H}_2\text{CNH}^{++}$ plus CH_4) via **TS1** (at 9.3 $\text{kJ}\cdot\text{mol}^{-1}$ below $\text{H}_2\text{CNH}^{++}$ plus CH_4). For the HCNH_2^{++} isomer, **A2** proceeds to **A4** via **TS3** (only 2.2 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants). However, for this isomer the pathway to **A4** requires first a reorientation to form the higher-energy adduct **A3** (8.8 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants) via **TS2** (at -8.6 $\text{kJ}\cdot\text{mol}^{-1}$ with respect to reactants). In both cases, **A4** can break apart to form CH_2NH_2^+ plus CH_3^+ , with products lying below the respective reagents by 62 (for HCNH_2^{++}) and 80 $\text{kJ}\cdot\text{mol}^{-1}$ (for $\text{H}_2\text{CNH}^{++}$).

Fig. 7: Enthalpies and reaction pathways for the H_2CNH_2^+ plus CH_4 (red) and HCNH_2^+ (black) plus CH_4 systems, both leading to CH_2NH_2^+ plus CH_3 products. Enthalpies (in $\text{kJ}\cdot\text{mol}^{-1}$) are defined with respect to the separated HCNH_2^+ plus CH_4 reactants. Calculations are at the MP2/cc-pVTZ//CCSD(T)/cc-pvTZ level of theory.

The relative energies of adducts and transition states with respect to the reagents can be rationalised by the fact that complex formation is driven by the charge-induced dipole interaction whereas the H atom transfer is driven by the radical moiety on the ion, as shown by the structure of products. This means that the structures **A1** and **TS1** are far more similar than **A2** and **TS3**, as in the latter case the ion needs to rotate relative to the CH_4 for the reaction to proceed. One can therefore expect a reduced efficiency for the HCNH_2^+ isomer. Due to the small energy difference between the HCNH_2^+ reagent and **TS3**, at low collision energies the reagent flux that overcomes the transition state to evolve into products is larger for H_2CNH_2^+ (going via **TS1**) than for HCNH_2^+ (going via **TS3**) and this could explain the higher CS for the H_2CNH_2^+ isomer at the low collision energies.

However, a question remains: all intermediates lie below the energy of the reactants, so how can we explain the increase in CS seen when increasing collision energy? (see **Fig. 6**). A possible explanation deals with the competition between the complex mediated mechanism (and associated reverse reactions towards reactants) and a direct H-stripping mechanism [Zabka00, Anderson95]. The complex-mediated mechanism proceeds via the van der Waals adducts and decreases with increasing collision energy, hence mostly contributing at low collision energies while the direct H stripping should be mostly flat with collision energy. At intermediate energies (E_{CM} 0.2-2 eV) one would therefore have a competition between complex formation and direct H stripping. In the HCNH_2^+ case the complex-mediated mechanism has a smaller contribution than for the other isomer due to the larger proportion of complexes returning to reagents (equivalent to missed collision, or apparently decreased cross section) rather than proceeding to products (reactive collision).

4.1 H atom transfer channel: comparisons with results from other reaction partners

H-atom transfer reactions to HCNH_2^{++} and $\text{H}_2\text{CNH}^{++}$ ions have been observed for other hydrocarbons, as well as CH_3OH , according to the following scheme (see the estimated reaction enthalpies from literature values in **Table 1**):

Table 1. Reaction enthalpies for reaction (3)

R-H	ΔH° with HCNH_2^{++} (eV) ^a	ΔH° with $\text{H}_2\text{CNH}^{++}$ (eV) ^a
CH_4	-0.67 ± 0.19 ^b	-0.83 ± 0.19 ^b
C_2H_4	-0.40 ± 0.24 ^c	-0.56 ± 0.24 ^c
C_3H_4 (allene)	-1.41 ± 0.22 ^d	-1.58 ± 0.22 ^d
C_3H_6 (propene)	-1.39 ± 0.21 ^e	-1.56 ± 0.21 ^e
CH_3OH	-0.65 ± 0.33 ^f	-0.82 ± 0.33 ^f

^a All values in the Table have been estimated using $\Delta_f H_{298}^\circ(\text{HCNH}_2^{++}) = 10.67 \pm 0.10$ eV, $\Delta_f H_{298}^\circ(\text{H}_2\text{CNH}^{++}) = 10.84 \pm 0.10$ eV [Nguyen94] and $\Delta_f H_{298}^\circ(\text{CH}_2\text{NH}_2^+) = +7.72 \pm 0.08$ eV [Holmes2006]

^b Using $\Delta_f H_{298}^\circ(\text{CH}_4) = -0.776 \pm 0.004$ eV [NIST ChemWeb] and $\Delta_f H_{298}^\circ(\text{CH}_3) = +1.510 \pm 0.008$ eV [NIST ChemWeb]

^c Using $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_3) = 3.10 \pm 0.05$ eV and $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_4) = 0.543 \pm 0.005$ eV [NIST ChemWeb]

^d Using $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_4) = 1.970 \pm 0.003$ eV [Argonne Active Thermochemical Table] and $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_3 \text{ propargyl}) = 3.513 \pm 0.041$ eV [NIST ChemWeb]

^e Using $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_6) = 0.210 \pm 0.003$ eV [Argonne Active Thermochemical Table] and assuming that the C_3H_5 allyl radical (CH_2CHCH_2) is produced, for which $\Delta_f H_{298}^\circ = 1.77 \pm 0.03$ eV [NIST ChemWeb]

^f Using $\Delta_f H_{298}^\circ(\text{CH}_3\text{OH}) = -2.12 \pm 0.10$ eV [NIST ChemWeb] and assuming that the CH_3O methoxy radical is produced, for which $\Delta_f H_{298}^\circ = +0.176 \pm 0.041$ eV [NIST ChemWeb]

The CS for reaction (3) as a function of the collision energy are given in **Fig. 8**. The three unsaturated species (C_2H_4 , C_3H_4 and C_3H_6) show a gradual decrease with increasing collision energy, whereas the saturated species (CH_4 and CH_3OH) both show a rise in CS at intermediate collision energies before plateauing at higher collision energies, with this feature being amplified for the HCNH_2^{++} isomer in both cases.

Fig. 8: Reactive cross sections (CSs) as a function of E_{CM} for the reaction of HCNH_2^+ (top) and H_2CNH^+ (bottom) with different R-H neutrals to give CH_2NH_2^+ products (m/z 30). The photon energy used is $E_{phot} = 11.48$ eV in all cases with the exception of HCNH_2^+ plus CH_3OH ($E_{phot} = 12.98$ eV) and HCNH_2^+ plus C_2H_4 ($E_{phot} = 1.98$ eV). Since in these cases the dependence of CS with E_{phot} is flat, such differences have no influence on the CS values as a function of E_{CM} .

The difference between the saturated and unsaturated species can be explained by the ability of the unsaturated species to form covalently-bound adducts, through which the reaction can proceed rapidly and often with little or no barrier. Whereas, for the saturated species, the chemistry at low collision energies is dominated by the formation of van der Waals complexes where there is a competition between dissociation into products and back-dissociations towards the reagents. At higher energies the reaction with saturated hydrocarbons will probably mainly proceed by a stripping mechanism.

The similarities in the CS trends with collision energy for CH_4 and CH_3OH support the hypothesis that they result from the competition between the two different mechanisms: direct H atom transfer and reaction proceeding via formation of an intermediate complex. Since the C-H and O-H bond dissociation enthalpies in CH_4 and CH_3OH are essentially identical (4.555 ± 0.001 and 4.54 ± 0.03 eV respectively [Blanksby03]), reaction enthalpies are not sufficient to explain the larger cross section observed for CH_3OH in the entire collision energy range, which is instead due to the presence of a dipole moment in methanol, thus leading to a more strongly bound adduct with CH_3OH than with CH_4 .

5. Conclusions

Dissociative photoionization experiments of suitable neutral precursors (cyclopropylamine and azetidine) using tuneable VUV photons in the range 10-14 eV and associated calculations confirm the possibility to produce the H_2CNH^{+} and HCNH_2^{+} radical cations independently and selectively. Both isomers react with CH_4 to exclusively give H_2CNH_2^+ plus CH_3^+ . Differences in the reactive cross sections as a function of the collision energy are interpreted, with the aid of theoretical calculations, in terms of competition between direct stripping and complex-mediated H atom transfer. Our study provides the first experimental measure of the absolute cross sections for the reactions of H_2CNH^{+} / HCNH_2^{+} with CH_4 .

Acknowledgements

We are grateful to the DESIRS beamline team for assistance during the synchrotron measurements and the technical staff of SOLEIL for the smooth running of the facility under projects n° 20180118 and 20190249. We thank prof. Marzio Rosi (University of Perugia, IT) for useful discussions on the theoretical calculations. This work was supported by the European Union's Horizon 2020 research and innovation programme "Astro-Chemistry Origins" (ACO), Grant No 811312. W.G. thanks the Swedish Research Council for a project grant (grant number 2019-04332). M.P. and J.Ž. acknowledge support from the Ministry of Education Youth and Sports of the Czech Republic (grant No. LTC20062). V.R. acknowledges funding for a PhD fellowship from the Dept. Physics, University of Trento.

Formatted: Font: (Default) Arial, 11 pt, English (United Kingdom), Check spelling and grammar

Bibliography

- [Alcaraz 2004] C. Alcaraz, C. Nicolas, R. Thissen, J. Žabka, and O. Dutuit, *J. Phys. Chem. A* 108 (2004) 9998–10009 doi: 10.1021/jp0477755
- [Anderson95] Y.-H. Chiu, H. Fu, J.-T. Huang, and S.L. Anderson, *J. Chem. Phys.* 102 (1995) 1199.
- [Anicich 2003]: V. G. Anicich, JPL-Publication-03-19 (2003) <http://hdl.handle.net/2014/7981>
- [ATcT] B. Ruscic, D. H. Bross, Active Thermochemical Tables (ATcT) values based on ver. 1.122e of the Thermochemical Network, Argonne National Laboratory (2019); available at ATcT.anl.gov
- [Audier2003] J. Chamot-Rooke, P. Mourgues, G. van der Rest, H.E. Audier, *Int. J. Mass Spectrom.* 226 (2003) 249–269
- [Baer2000] T. Baer, Y. Song, J. Liu, W. Chen, C. Y. Ng, *Faraday Discuss.* 115 (2000) 137–145
- [Balucani19] C. H. Yuen, M. A. Ayouz, N. Balucani, C. Ceccarelli, I. F. Schneider and V. Kokoouline, *MNRAS* 484 (2019) 659–664
- [Benson1976] Benson S. W. “Thermochemical Kinetics”; Wiley-Interscience: New York, 1976.
- [Blanksby03] S.J.Blanksby, G. B. Ellison, *Acc. Chem. Res.* 36 (2003) 4, 255–263
- [Bohme2009] A. Shayesteh, V. V. Lavrov, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* 113 (2009) 19, 5602–5611 doi:10.1021/jp900671c
- [Bouchoux1998] G. Bouchoux, C. Alcaraz, O. Dutuit, and M. T. Nguyen, *J. Am. Chem. Soc.* 120 (1998) 152–160
- [Bouchoux2000] G. Bouchoux, B. Gaudin, D. Leblanc, M. Yáñez and O. Mó, *Int. J. Mass Spectrom.* 199 (2000) 59–69
- [Burgers1984] P.C. Burgers, J.L. Holmes and J.K. Terlouw, *J. Am. Chem. Soc.* 106 (1984) 2762
- [Castrovilli2014] 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.* 25 (2014) 351–367
- [Cunha 2015] Cunha de Miranda, B., Romanzin, C., Chefdeville, S., Vuitton, V., Žabka, J., Polášek, M., et al. *J. Phys. Chem. A* 119 (2015) 6082–6098 doi: 10.1021/jp512846v
- [Chupka71] W.A. Chupka, *J. Chem. Phys.* 54 (1971) 1936–1947
- [dePretis2009] G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini *Chem. Eur. J.* 15 (2009) 4248–4252 DOI: 10.1002/chem.200802581
- [Dietl2013] N. Dietl, A. Troiani, M. Schlangen, O. Ursini, G. Angelini, Y. Apeloig, G. de Petris and H. Schwarz, *Chem. Eur. J.* 19 (2013) 6662–6669 DOI: 10.1002/chem.201204157
- [Eckhardt2018] A. K. Eckhardt and P. R. Schreiner, *Angew. Chem. Int. Ed.* 57 (2018) 5248 – 5252
- [GAUSSIAN] Gaussian 09, Revision D.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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[Holmes1992] J.L. Holmes, F.P. Lossing and P.M. Mayer, Chem. Phys. Lett. 198 (1992) 211.

[Holmes2006] Holmes J., Aubry, C., and Mayer, P. Assigning Structures to Ions in Mass Spectrometry (2006) CRC Press, Taylor & Francis Group, Boca Raton FL (USA)

[Holzmeier2013] F. Holzmeier, M. Lang, K. Hader, P. Hemberger, and I. Fischer J. Chem. Phys. 138 (2013) 214310

[Lavvas2008] P. Lavvas, A. Coustenis, and I. Vardavas Planet. Space Sci. 56 (2008) 67

[Mercier 2000] Mercier, B; Compin, M; Prevost, C; et al. J. Vacuum Sci. Technol. A-VACUUM SURFACES AND FILMS 18 (2000) 2533-2541 DOI: 10.1116/1.1288196

[Minnhagen 1973] L. Minnhagen, J. Opt. Soc. Am. 63 (1973) 1185–1198
DOI:10.1364/JOSA.63.001185

[Nahon 2012] L. Nahon, N. de Oliveira, G.A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde and F. Polack, J. Synchrotron Rad. 19 (2012) 508–520. doi: 10.1107/S0909049512010588

[Nguyen1994] M. T. Nguyen, J. Rademakers, J.M.L. Martin, Chem. Phys. Lett. 221 (1994) 149

[NIST ASD] NIST Atomic Spectra Database. Available: <http://physics.nist.gov/asd>

[NIST Chem] NIST Chemistry WebBook, NIST Standard Reference Data Base Number 69, Gaithersburg, MD: National Institute of Standards and Technology

[Polce1997] M.J. Polce Y. Kim, C. Wesdemiotis, Int. J. Mass Spectrom. Ion Proc. 167/168 (1997) 309-315

[Ryan1995] M. F. Ryan, A. Fiedler, D. Schroeder, H. Schwarz, J. Am. Chem. Soc. 117 (1995) 7, 2033–2040 doi: 10.1021/ja00112a017

[Schroder1995] D. Schröder, and H. Schwarz, Angew. Chem. Int. Ed. Engl., 34 (1995) 1973-
doi:10.1002/anie.199519731

[Schwarz2012] N. Dietl, M. Schlangen, and H. Schwarz Angew. Chem. Int. Ed. 51 (2012) 5544 – 5555

[Schwarz2015] H. Schwarz, Chem. Phys. Lett. 629 (2015) 91–101

[Schwarz2017] H. Schwarz, P. Gonzalez-Navarrete, J.L. Li, M. Schlangen, X.Y. Sun, T. Weiske, S.D. Zhou, Organometallic 36 (2017) 8-17 DOI: 10.1021/acs.organomet.6b00372

[Shebanits2016] O. Shebanits, J.-E. Wahlund, N. J. T. Edberg, F. J. Cray, A. Wellbrock, D. J. Andrews, E. Vigren, R. T. Desai, A. J. Coates, K. E. Mandt, and J. H. Waite Jr, J. Geophys. Res. Space Physics 121 (2016) 10075–10090.

[Skouteris2015] D. Skouteris, N. Balucani, N. Faginas-Lago, S. Falcinelli, and M. Rosi A&A 584 (2015) A76

[Spartan] Spartan; Wavefunction Inc.: 18401 Von In Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A., 1994, www.wavefun.com.

[Sundelin21] D. Sundelin, D. Ascenzi, V. Richardson, C. Alcaraz, M. Polášek, C. Romanzin, R. Thissen, P. Tosi, J. Žabka and W. Geppert submitted to Chem. Phys. Lett. (2021)

[Tarasenko1986] N.A. Tarasenko, A.A. Tishenkov, V.G. Zaikin, V.V. Volkova and L.E. Gusef'nikov, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 2397

[Teloy 1974] E. Teloy, D. Gerlich, Chem. Phys. 4 (1974) 417 - 427.

[Traeger1981] J. C. Traeger and R. G. McLoughlin, J. Am. Chem. Soc. 103 (1981) 3647-3652

[Viggiano2020] B.C. Sweeny, H.Q. Pan, A. Kassem, J.C. Sawyer, S.G. Ard, N.S. Shuman, A.A. Viggiano, S. Brickel, O.T. Unke, M. Upadhyay, M. Meuwly, Phys.Chem.Chem.Phys. 22 (2020) 8913-8923. DOI 10.1039/d0cp00668h

[Vuitton2006] V. Vuitton, R. V. Yelle, and V. G. Anicich Astrophys. J. 647 (2006) L175

[Vuitton2007] V. Vuitton, R.V. Yelle, M.J. McEwan Icarus 191 (2007) 722–742

[Vuitton2019] V. Vuitton, R.V. Yelle, S.J. Klippenstei, S.M. Hörst, P. Lavvas, Icarus 324 (2019) 120–197

[Westlake2014]. J.H. Westlake, J.H. Waite, N. Carrasco, M. Richard, T. Cravens, J. Geophys. Res. A119 (2014) 5951–5963

[Zabka00] J. Zabka, O. Dutuit, Z. Dolejšek, J. Polach and Z. Herman Phys. Chem. Chem. Phys. 2 (2000) 781-786

The reactivity of methanimine radical cation ($\text{H}_2\text{CNH}^{+\bullet}$) and its isomer aminomethylene ($\text{HCNH}_2^{+\bullet}$) with methane

V. Richardson^a, C. Alcaraz^{b,c}, W. D. Geppert^d, M. Polášek^e, C. Romanzin^{b,c}, D. Sundelin^d, R. Thissen^{b,c}, P. Tosi^a, J. Žabka^e and D. Ascenzi^{a*}

^a Department of Physics, University of Trento, Via Sommarive 14 – 38123 Italy

^b Université Paris-Saclay, CNRS, Institut de Chimie Physique, UMR8000, 91405 Orsay, France

^c Synchrotron SOLEIL, L'Orme des Merisiers, F-91192 Saint Aubin, Gif-sur-Yvette, France

^d Department of Physics, Stockholm University, Roslagstullsbacken 21, 10691 Stockholm, Sweden

^e J. Heyrovský Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, Prague 8, 18223 Czech Republic

* corresponding author: e-mail daniela.ascenzi@unitn.it phone: +39 0461 281693

Abstract

Experimental and theoretical studies are presented on the reactions of the isomeric radical cations $\text{H}_2\text{CNH}^{+\bullet}$ and $\text{HCNH}_2^{+\bullet}$ with CH_4 . Ionic isomers were generated selectively by VUV dissociative photoionization of azetidine and cyclopropylamine precursors respectively. Both exclusively give H_2CNH_2^+ plus $\text{CH}_3^\bullet$ as products, but differences are observed related to a competition between stripping and complex-mediated H-transfer. Astrochemical implications for Titan's atmosphere are briefly discussed, where the presence of methanimine (H_2CNH), a key prebiotic molecule and a potential precursor for tholins, is proposed on the basis of atmospheric models and the observation of CH_2NH_2^+ ions in Cassini mass spectrometric data.

Keywords: interstellar medium; rate constants; ion-molecule reactions; astrochemistry; molecular astrophysics; Titan's atmosphere; methane activation; isomer; methanimine; aminomethylene

1. Introduction

The reactivity of methane with a range of ions has been the focus of several experimental and theoretical studies [Schroder1995; Ryan1995; Bohme2009] due to its relevance to a variety of environments and to the interest in the activation of C-H bonds in saturated species. The activation of methane has been studied via reaction with cations and radicals [dePretis2009, Dietl2013, Schwarz2015, Schwarz2017, Viggiano2020] with two mechanisms being proposed: direct hydrogen transfer and reaction via intermediate complexes.

Here, we focus on the reaction of CH_4 with the two lowest energy isomers of $[\text{CH}_3\text{N}]^{+\bullet}$: $\text{H}_2\text{CNH}^{+\bullet}$ and $\text{HCNH}_2^{+\bullet}$. Though they both contain a radical moiety and a cationic nitrogen, $\text{H}_2\text{CNH}^{+\bullet}$ has a radical cation character while the $\text{HCNH}_2^{+\bullet}$ isomer is distonic, thus allowing for a comparison of the chemistry of the two functionalities independently, as well as in combination. Additionally, these are the two simplest imine cations, and so their reactions should provide insight into the reactivity of this functional group, which has been identified as a potential core building block in the formation of amino acids [Aponte and Elsila 2017].

From an astrochemical perspective the title reaction is relevant to the chemistry of methanimine $\text{H}_2\text{C}=\text{NH}$ and its related ions in Titan's atmosphere. Here, the presence of considerable amounts

of neutral methanimine has been proposed by models [Vuitton2019, Lavvas2008] on the basis of an intense peak at m/z 30 present in the mass spectrum from the Ion Neutral Mass Spectrometer of Cassini and attributed to protonated methanimine CH_2NH_2^+ [Vuitton2006, Vuitton2007, Balucani19].

Such models have predicted only a minor presence of $\text{H}_2\text{CNH}^{++}/\text{HCNH}_2^{++}$ in Titan's atmosphere ($1.1 \times 10^{-2} \text{ cm}^{-3}$ [Vuitton2007]) though this could be due to their high reactivity and, consequently, fast destruction. A theoretical study [Skouteris2015] has indicated that the barriers for bond-forming reactions starting from neutral methanimine are unfeasibly high for the low temperature environments of Titan, but the formation of covalently bound adducts from the ionic form is in many cases barrierless.

The idea has therefore been put forward that methanimine radical cations might be the basis for methanimine polymerization [Skouteris2015], eventually leading to the build up to detected complex ions [Westlake2014, Vuitton2019]. These, in turn, may account for the formation of the Titan nitrogen-rich aerosols. Since $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} are stable species separated by a high isomerization barrier [Nguyen1994], the reactivity of both isomers should be addressed, as well as the possibility for their isomerization. As CH_4 is the most abundant hydrocarbon in Titan's atmosphere, it is a logical starting point for reactivity studies.

In this paper we describe an experimental method to selectively produce the title ions by dissociative photoionization of cyclopropylamine and azetidine using tuneable VUV synchrotron radiation. In **Sec. 3** experimental and theoretical results on the dissociative photoionization of the precursors are presented and potential contaminations by isobaric ions are discussed. In **Sec. 4** results from the reactions of $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} cation isomers with CH_4 are presented, together with computational data to help rationalise the observations. In the accompanying paper [Sundelin21] the reactivity with C_2H_4 is presented.

2. Experimental and computational Sections

2.1 Experimental set-up

Experiments were performed using the CERISES apparatus [Alcaraz 2004; Cunha 2015] at the DESIRS beamline [Nahon2012] of the SOLEIL synchrotron radiation facility. CERISES is a guided ion beam tandem mass spectrometer composed of two octopoles located between two quadrupole mass filters that permits investigation of bi-molecular reactions of mass-selected ions. By measuring the yields of parent- and product-ions, absolute cross sections (CS) are derived as a function of both photon and collision energy.

$[\text{CH}_3\text{N}]^{++}$ isomers were produced by dissociative photoionization of suitable gaseous precursors (see **Section 3**) introduced at roughly 10^{-6} mbar in the ion source. CH_4 was introduced in the reaction cell at a dynamic pressure of 2×10^{-7} bar, which guarantees operation close to a single collision regime, reduces secondary reactions and limits the parent ion attenuation to less than 10%. The absolute pressure was measured using the MKS 398H differential manometer.

The photon energies (E_{phot}) used to generate $[\text{CH}_3\text{N}]^{++}$ ions are in the range of 9.5–14 eV. Monochromator slits were set to define photon energy resolution of 20 to 40 meV. The gas filter [Mercier 2000] of the beamline used Argon to remove photons above 15.7 eV. The absolute scale of the photon energy was based on absorption lines of Argon around 11.828 and 14.304 eV [Minnhagen 1973, NIST ASD], with systematic shifts of about 10–20 meV above their tabulated values.

The mass filter resolution was adjusted in order to maximize signal and provide sufficient removal of ions at adjacent mass units. A pollution of ~0.01% of neighbouring ions for Q1 and ~0.1% for Q2 is estimated at the lowest collision energy, which for the later increases to 1.2% at an acceleration potential of 20 V. Collision energy was set by the difference between the ion source and the reaction cell potentials. This was determined by the retarding potential method [Teloy 1974], giving a parent beam FWHM of 0.4 eV in the LAB frame. By changing the potentials of the reaction cell and all subsequent elements up to 20V, the collision energy can be spanned from ~0.06 eV up to ~10 eV in the centre-of-mass frame (E_{CM}).

Acquisitions, both for photon and collision energy scans, were performed by counting signal for all ionic species at a single point before moving to the next one. This drastically reduces effects of pressure drifts in source and reaction cell.

2.2 Theoretical Methodology

Relevant structures in the PES describing the dissociative ionisation of the cyclopropylamine and azetidine precursors were performed using Wavefunction's Spartan '18 suite [Spartan]. For stable structures, corresponding to energy minima, calculations were conducted at the G3 level, which is a combination of Hartree-Fock and wave function-based electron correlation methods, with the output being the enthalpy of formation at 298 K. For transition states, calculations were conducted at the ω B97X-D/cc-pVTZ level. ω B97X-D is a Range Separated Hybrid Generalized Gradient Approximation functional, which uses Grimme corrections (-D) in order to account for dispersive interactions. Cc-pVTZ refers to the Correlation consistent polarized Valence Triple Zeta basis set, which is a triple-zeta basis set intended specifically for use in correlated calculations.

Calculations of the reaction mechanisms of $\text{HCNH}_2^{++}/\text{H}_2\text{CNH}^{++}$ plus CH_4 were performed using GAUSSIAN [GAUSSIAN]. Intermediate structures, *i.e.* minima and transition states, were calculated at the MP2/6-31G*, MP2/6-311++G** and MP2/cc-pVTZ levels. The identity of transition states and minima were checked by frequency calculations and zero-point energy corrections were employed to the obtained energies. IRC calculations were performed at the MP2/6-31G* level to ensure that the transition states connect the correct minima. Energy calculations were carried out for all stationary points at the CCSD(T)/6-311++G** and CCSD(T)/cc-pVTZ levels with zero-point energy corrections taken from the MP2/6-311++G** and MP2/cc-pVTZ levels respectively. Reactants and product geometries and energies were also calculated at the same level (including zero-point energy corrections) and their energies subtracted from the optimizations of the transition states and minima, resulting in the relative energies E_{rel} . Full results are given in the **Supplementary Information 1** (Tables 1-4 and Figs. 1-3).

3. Results and discussion: generation of different $[\text{CH}_3\text{N}]^{++}$ isomers

The HCNH_2^{++} and $\text{H}_2\text{CNH}^{++}$ isomers have been generated via dissociative photoionization of cyclopropylamine ($c\text{-C}_3\text{H}_5\text{NH}_2$) and azetidine ($c\text{-CH}_2\text{CH}_2\text{CH}_2\text{NH}$), respectively, as proposed in [Audier03, Polce97, Burgers84]:

(1b)

3.1 Dissociative photoionization of cyclopropylamine

The photoionization and subsequent H ejection from cyclopropylamine has been studied both experimentally and theoretically [Bouchoux1998, Bouchoux2000] where an ionization energy IE for $c\text{-C}_3\text{H}_5\text{NH}_2$ was given as 8.78 ± 0.03 eV. These authors demonstrated that the cyclic structure ring-opens upon ionization at threshold to give $\text{CH}_2\text{CH}_2\text{CHNH}_2^{++}$. In Fig. 1 calculations are presented on the energetics of the fragmentation pathways of this ion over the studied photon energy range. A comparison with literature data is given in Table S1 of the Supplementary Information 2.

The photoionization efficiency (PIE) curves (*i.e.* ion yields as a function of photon energy) for the dissociative ionization products of cyclopropylamine at m/z 29 (sum of HCNH_2^{++} and C_2H_5^+), m/z 28 (sum of HCNH^+ and C_2H_4^+) and m/z 30 (H_2CNH_2^+) are shown in Fig. 2, where the observed appearance energies (AEs) are reported. To evaluate the AEs the method of linear threshold extrapolations of the PIE curves is used [Chupka71, Traeger1981, Castrovilli2014].

However, the PIE curve at m/z 29 does not show any well-defined onset but rather a curved threshold region that could not be fitted with a linear regression. In this case the experimental AE is obtained from the actual onset of the PIE curve, taking the first point above noise level as a rough estimate. We refrain from transforming experimental AEs into reaction enthalpies/energies since it will require accounting for Franck Condon factors, the presence of excited states of the parent ion and the thermal enthalpy correction term. This is beyond the scope of the paper, which doesn't aim to measure the heat of formation of $\text{H}_2\text{CNH}^{++}$ and HCNH_2^{++} ions but rather their reactivity. We also note that the AE of the parent ion (m/z 57) and the H loss channel (m/z 56) are at 8.7 ± 0.1 eV and 9.2 ± 0.1 eV respectively (data not shown), in agreement with previous studies [Bouchoux et al. 1998 ; Bouchoux et al. 2000].

Dissociative ionization to give HCNH_2^{++} plus C_2H_4 via the open structure $\text{CH}_2\text{CH}_2\text{CHNH}_2^{++}$ has a calculated reaction enthalpy of 10.41 eV, in agreement with the 10.42 ± 0.11 eV literature value [Nguyen1994]. Our experimental AE (corresponding to the first point above noise level, see inset a) in Fig. 2) of 10.2 ± 0.1 eV is lower than previous value of 11.00 ± 0.05 eV [Burgers1984] obtained via dissociative electron ionization with energy selected electrons. The identification of the fragment ion as the aminomethylene isomer has been previously proposed on the basis of collisionally activated dissociation, metastable ion mass spectra and charge reversal experiments [Polce97, Burgers84].

Production of HCNH^+ in combination with C_2H_5^+ may proceed via a [1, 4] H shift to the $\text{CH}_3\text{CH}_2\text{CHNH}^+$ intermediate structure. Our calculations give an overall reaction enthalpy of 10.22 eV, in agreement with the 10.30 ± 0.18 eV that can be estimated from values reported in [Holmes2006]. The experimental AE of 10.40 ± 0.26 eV for m/z 28 (see inset b) in Fig. 2) is consistent with the opening of this fragmentation channel, which has an AE close to the HCNH_2^{++} isomer. Given that the yield of m/z 28 fragment from cyclopropylamine is more intense than that

for m/z 29 (see Fig. 2) we considered the effect of isobaric impurities due to $\text{H}^{13}\text{CNH}^+$ when mass selecting ions at m/z 29 to carry out reactivity experiments (see the following).

Fig. 1: Scheme of the most relevant dissociations pathways upon ionization of cyclopropylamine. Enthalpy differences (in eV, relative to the cyclopropylamine neutral) are calculated at the G3 level for the PES minima and at DFT level (ω B97X-D with cc-pVTZ basis set) for the transition states.

The formation of the isobaric cation C_2H_5^+ in combination with the iminomethyl radical HCNH^+ is shown to be a higher energy channel from the same intermediate structure, with our computational value of 11.39 eV being in good agreement with the literature value of 11.35 ± 0.03 eV [Baer2000, ATcT]. The alternative dissociation channel producing C_2H_5^+ plus H_2CN^+ (methylenamidogen radical) is less endothermic ($\Delta H^\circ = 11.02$ eV) but it is hampered by an energy barrier (TS state located at 11.68 eV). Hence we can not exclude the production of C_2H_5^+ as a contaminant of the HCNH_2^{++} isomer at photon energies larger than ~ 11.4 eV. Indirect evidence for the formation of C_2H_5^+ at high photon energies is discussed in the accompanying paper [Sundelin21], where the reactivity of m/z 29 from dissociative photoionization of cyclopropylamine against C_2H_4 is reported. There, the appearance of an intense product at m/z 41 at photon energy ~ 12.4 eV, is attributed to the presence of C_2H_5^+ , which is known to react readily with ethylene to give C_3H_5^+ plus CH_4 [Anicich93].

Direct dissociation of $\text{CH}_2\text{CH}_2\text{CHNH}_2^{++}$ to give $\text{C}_2\text{H}_4^{++}$ plus HCNH_2 is calculated as being a more endothermic channel with an enthalpy of 12.75 eV, in good agreement with the literature value of 12.73 ± 0.03 eV [NIST Chem, Nguyen1994]. Formation of $\text{C}_2\text{H}_4^{++}$ is therefore expected to occur only at high photon energies.

Production of aminomethyl cation CH_2NH_2^+ in combination with C_2H_3^+ requires a rearrangement (a [1, 2] H shift) into $\text{CH}_2\text{CHCH}_2\text{NH}_2^{++}$, from which dissociation proceeds barrierlessly. The

calculated enthalpy of 10.02 eV matches the literature value of 10.02 ± 0.14 [Holmes2006, NIST Chem] as does our experimental AE of 10.20 ± 0.05 eV.

In summary, dissociative photoionization of cyclopropylamine allows for the production of the HCNH_2^{++} isomer with $\text{AE} = 10.2 \pm 0.1$ eV and potential contamination from C_2H_5^+ limited to high photon energies ($E_{\text{phot}} > 11.4$ eV).

Fig. 2: PIE curves for the dissociative photoionization of cyclopropylamine to give ions at m/z 29 (red data), m/z 28 (blue data) and m/z 30 (black data). Insets **a)** **b)** and **c)** show zooms in the threshold region for the corresponding m/z values. Dashed lines are the linear extrapolations used to extract the experimental AEs, when possible.

3.2 Dissociative photoionization of azetidine

The production of $\text{H}_2\text{CNH}^{++}$ via a $[2 + 2]$ cycloreversion reaction of azetidine has been proposed previously [Burgers1984] where the AE for m/z 29 ions was measured via energy selected electrons to be 10.46 ± 0.05 eV. The identification of the charged fragment as $\text{H}_2\text{CNH}^{++}$ has been proposed on the basis of collisionally activated dissociation, metastable ion mass spectra and charge reversal experiments [Burgers1984, Polce1997]. A photoionization-mass spectrometry investigation of azetidine measured the AE for this channel as 10.32 ± 0.08 eV [Tarasenko 1986; Holmes1992] and for the formation of HCNH^+ as 9.98 ± 0.02 eV.

To the best of our knowledge the full dissociative ionization of azetidine has not been investigated experimentally or theoretically. A scheme of the most relevant dissociation pathways from calculations is presented in Fig. 3 and a comparison with literature data is given in Table S2 of the Supplementary Information 2. The PIE curves for the dissociative ionization products of azetidine at m/z 29 (sum of HCNH_2^{++} and C_2H_5^+) and m/z 28 (sum of HCNH^+ and $\text{C}_2\text{H}_4^{++}$) are presented in Fig. 4, where AEs are derived as discussed in the previous section. We note that

the AE of the m/z 57 parent ion (8.7 ± 0.1 eV) and the m/z 56 H loss channel (9.2 ± 0.1 eV), data not shown, are in agreement with previous work [Tarasenko 1986].

Fig. 3: Scheme of the most relevant dissociations pathways upon ionization of azetidine. Enthalpy differences (in eV, relative to the azetidine neutral) are calculated at the G3 level for the PES minima and at DFT level (ω B97X-D with cc-pVTZ basis set) for the transition states

Production of the target ion $\text{H}_2\text{CNH}^{++}$ in combination with C_2H_4 requires a rearrangement to the open structure $\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ from which dissociation proceeds barrierlessly with an overall calculated reaction enthalpy of 10.35 eV, in excellent agreement with the value 10.36 ± 0.16 eV [Nguyen1994]. Our experimental AE of 10.2 ± 0.1 eV (corresponding to the first point above noise level, see inset a) in Fig. 4) is consistent both with these calculations and with previous experimental values [Tarasenko 1986; Holmes1992].

Production of HCNH^+ in combination with C_2H_5^+ proceeds by a [1, 4] H shift from $\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ to yield $\text{CH}_3\text{CH}_2\text{NHCH}^{++}$. The latter fragments into products with a barrier of 10.14 eV. Our experimental AE for m/z 28 of 10.22 ± 0.06 eV is in fair agreement both with the computational value and the literature reaction enthalpy of 10.08 ± 0.22 eV [Holmes2006]. Similarly to the cyclopropylamine case, this fragmentation channel opens at similar E_{phot} as the $\text{H}_2\text{CNH}^{++}$ isomer.

The formation of C_2H_5^+ in combination with HCNH^+ is a more endothermic channel which proceeds via $\text{CH}_3\text{CH}_2\text{NHCH}^{++}$ with a calculated reaction enthalpy of 11.17 eV (in good agreement with the literature estimate of 11.13 ± 0.08 eV [Baer2000, ATcT]). The formation of C_2H_5^+ in combination with H_2CN^+ has a smaller reaction enthalpy (10.80 eV) but it is inhibited by a reaction barrier (TS located at 11.30 eV). Hence the production of C_2H_5^+ as a contaminant of the $\text{H}_2\text{CNH}^{++}$ isomer should be considered when working at photon energies above ~ 11 eV.

$\text{CH}_2\text{NHCH}_2\text{CH}_2^{++}$ can also fragment to give $\text{C}_2\text{H}_4^{++}$ plus H_2CNH with a reaction enthalpy of 10.97 eV, in good agreement with the literature value of 10.95 ± 0.23 eV [NIST ChemWeb, Holmes1992, ATcT]. The formation of $\text{C}_2\text{H}_4^{++}$ from azetidine is therefore expected to have a lower AE than from cyclopropylamine. In the azetidine case, one should therefore consider the effect of isobaric impurities due to $^{13}\text{CCH}_4^{++}$ as well as $\text{H}^{13}\text{CNH}^+$ when mass selecting ions at m/z 29. However, since the yield of m/z 29 fragment from azetidine is more intense than that for m/z 28 with the exception of the threshold region (see Fig. 4), any contamination is expected to be minor.

Fig. 4 PIE curves for the dissociative photoionization of azetidine to give ions at m/z 29 (red data) and 28 (blue data). Insets **a**) and **b**) show zooms in the threshold region for the corresponding m/z values. Dashed line is the linear extrapolation used to extract the experimental AEs, when possible.

4. Results and discussion: reactivity experiment

To exclude any interference from isobaric contaminants arising from ^{13}C ($\text{H}^{13}\text{CNH}^+$ and $^{13}\text{CCH}_4^{++}$) at m/z 29, we have performed preliminary experiments with CH_4 selecting the m/z 28 ions (a combination of HCNH^+ and $\text{C}_2\text{H}_4^{++}$) from dissociative photo-ionization of cyclopropylamine and azetidine. We observe no reactivity (i.e. CS smaller than $0.02 \text{ \AA}^2$), in agreement with literature: both HCNH^+ and $\text{C}_2\text{H}_4^{++}$ are unreactive towards methane ($k < 1.00 \cdot 10^{-13}$ [Anicich 2003]). C_2H_5^+ is known to have a small reactivity with CH_4 ($k = 9 \cdot 10^{-14}$ [Anicich 2003] leading to C_3H_7^+ (m/z 43) plus H_2). However, no ion counts at m/z 43 are detected upon reaction of m/z 29 from both precursors, even at the photon energies at which C_2H_5^+ production is energetically possible.

Upon reaction with CH_4 both isomers show a unique product at m/z 30, which corresponds to H abstraction from methane to give CH_2NH_2^+ plus $\text{CH}_3\cdot$:

Only **2a** has been studied in the literature [Audier2003] (where no values of absolute rate constants or CS are given) and the main channel is H atom abstraction, in agreement with our results. Calculations as part of this study indicate that reactions (**2a**) and (**2b**) are exothermic by 0.64 and 0.83 eV respectively, in good agreement with literature values (see **Table S3** in the **Supplementary Information 2**).

The CS dependences on photon energy (see **Fig. 5**) are similar for both isomers. Data is noisy just above threshold due to low parent ion signals but it shows that CSs are approximately constant as a function of photon energy at both collision energies and for both isomers. Given the exothermicities of **2a** and **2b**, it should be expected that they show little dependence on the (here unknown) internal energy of the reactant ion, supporting this observation.

Fig. 5: Reactive CSs as a function of E_{phot} for the reaction of HCNH_2^{++} (top) and $\text{H}_2\text{CNH}^{++}$ (bottom) with CH_4 at fixed collision energies (E_{CM}) indicated in the figure. The vertical dashed lines show the photon energies at which spectra as a function of E_{CM} have been collected (see Fig. 6)

Fig. 6 shows the collision energy trends of the CSs probed at fixed $E_{\text{phot}} = 11.48$ eV (plus $E_{\text{phot}} = 11.98$ eV only for HCNH_2^{++}). For the HCNH_2^{++} isomer, apart from a contribution at $E_{\text{CM}} < 0.1$ eV, the CS increases with increasing E_{CM} (up to about 2 eV), with a plateau at higher E_{CM} . For $\text{H}_2\text{CNH}^{++}$ the CS is larger than for HCNH_2^{++} at low E_{CM} with a more gentle rise in the 0.2-2 eV range.

Fig. 6: Reactive CSs as a function of collision energy E_{CM} for the reaction of HCNH_2^{+*} (top) and $\text{H}_2\text{CNH}^{+*}$ (bottom) with CH_4 measured at fixed photon energies (E_{phot}). The dotted lines indicate the collision energies at which spectra have been taken as a function of E_{phot} (see Fig. 5).

Calculations have identified van der Waals adducts for the two reacting isomers through which reaction can proceed (see Fig. 7 for a sketch of the pathways). The reactant radical cations are both planar molecules with a doublet ground state. Previous calculations [Nguyen1994] at the RCCSD(T) level of theory give the electronic energy of $\text{H}_2\text{CNH}^{+*}$ as 23–24 $\text{kJ}\cdot\text{mol}^{-1}$ higher than HCNH_2^{+*} . This value reduces to 16 $\text{kJ}\cdot\text{mol}^{-1}$ when taking the vibrational zero-point energies and thermal corrections into account, at both 0 and 298 K. Our calculations give a difference of $\sim 18 \text{ kJ}\cdot\text{mol}^{-1}$ for the energies of the two isomers, in good agreement with previous results. In the following discussion energies are given (in $\text{kJ}\cdot\text{mol}^{-1}$).

For both isomers, the lowest energy complex is formed barrierlessly and corresponds to N-terminal approach of the ion to the neutral. For $\text{H}_2\text{CNH}^{+*}$ this structure, **A1**, is 24.8 $\text{kJ}\cdot\text{mol}^{-1}$ below the energy of the reactants, while for HCNH_2^{+*} the corresponding structure **A2** lies 18.2 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants. **A1** is able to transfer an H from the methane to the ion to give **A4** (which is common to both isomers and lies 107.2 $\text{kJ}\cdot\text{mol}^{-1}$ below $\text{H}_2\text{CNH}^{+*}$ plus CH_4) via **TS1** (at 9.3 $\text{kJ}\cdot\text{mol}^{-1}$ below $\text{H}_2\text{CNH}^{+*}$ plus CH_4). For the HCNH_2^{+*} isomer, **A2** proceeds to **A4** via **TS3** (only 2.2 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants). However, for this isomer the pathway to **A4** requires first a reorientation to form the higher-energy adduct **A3** (8.8 $\text{kJ}\cdot\text{mol}^{-1}$ below the reactants) via **TS2** (at -8.6 $\text{kJ}\cdot\text{mol}^{-1}$ with respect to reactants). In both cases, **A4** can break apart to form CH_2NH_2^+ plus $\text{CH}_3^{\cdot}$, with products lying below the respective reagents by 62 (for HCNH_2^{+*}) and 80 $\text{kJ}\cdot\text{mol}^{-1}$ (for $\text{H}_2\text{CNH}^{+*}$).

Fig. 7: Enthalpies and reaction pathways for the H_2CNH_2^+ plus CH_4 (red) and HCNH_2^+ (black) plus CH_4 systems, both leading to CH_2NH_2^+ plus CH_3 products. Enthalpies (in $\text{kJ}\cdot\text{mol}^{-1}$) are defined with respect to the separated HCNH_2^+ plus CH_4 reactants. Calculations are at the **MP2/cc-pVTZ//CCSD(T)/cc-pvTZ** level of theory.

The relative energies of adducts and transition states with respect to the reagents can be rationalised by the fact that complex formation is driven by the charge-induced dipole interaction whereas the H atom transfer is driven by the radical moiety on the ion, as shown by the structure of products. This means that the structures **A1** and **TS1** are far more similar than **A2** and **TS3**, as in the latter case the ion needs to rotate relative to the CH_4 for the reaction to proceed. One can therefore expect a reduced efficiency for the HCNH_2^+ isomer. Due to the small energy difference between the HCNH_2^+ reagent and **TS3**, at low collision energies the reagent flux that overcomes the transition state to evolve into products is larger for H_2CNH_2^+ (going via **TS1**) than for HCNH_2^+ (going via **TS3**) and this could explain the higher CS for the H_2CNH_2^+ isomer at the low collision energies.

However, a question remains: all intermediates lie below the energy of the reactants, so how can we explain the increase in CS seen when increasing collision energy? (see **Fig. 6**). A possible explanation deals with the competition between the complex mediated mechanism (and associated reverse reactions towards reactants) and a direct H-stripping mechanism [Zabka00, Anderson95]. The complex-mediated mechanism proceeds via the van der Waals adducts and decreases with increasing collision energy, hence mostly contributing at low collision energies while the direct H stripping should be mostly flat with collision energy. At intermediate energies (E_{CM} 0.2-2 eV) one would therefore have a competition between complex formation and direct H stripping. In the HCNH_2^+ case the complex-mediated mechanism has a smaller contribution than for the other isomer due to the larger proportion of complexes returning to reagents (equivalent to missed collision, or apparently decreased cross section) rather than proceeding to products (reactive collision).

4.1 H atom transfer channel: comparisons with results from other reaction partners

H-atom transfer reactions to HCNH_2^{++} and $\text{H}_2\text{CNH}^{++}$ ions have been observed for other hydrocarbons, as well as CH_3OH , according to the following scheme (see the estimated reaction enthalpies from literature values in **Table 1**):

Table 1. Reaction enthalpies for reaction (3)

R-H	ΔH° with HCNH_2^{++} (eV) ^a	ΔH° with $\text{H}_2\text{CNH}^{++}$ (eV) ^a
CH_4	-0.67 ± 0.19 ^b	-0.83 ± 0.19 ^b
C_2H_4	-0.40 ± 0.24 ^c	-0.56 ± 0.24 ^c
C_3H_4 (allene)	-1.41 ± 0.22 ^d	-1.58 ± 0.22 ^d
C_3H_6 (propene)	-1.39 ± 0.21 ^e	-1.56 ± 0.21 ^e
CH_3OH	-0.65 ± 0.33 ^f	-0.82 ± 0.33 ^f

^a All values in the Table have been estimated using $\Delta_f H_{298}^\circ(\text{HCNH}_2^{++}) = 10.67 \pm 0.10$ eV, $\Delta_f H_{298}^\circ(\text{H}_2\text{CNH}^{++}) = 10.84 \pm 0.10$ eV [Nguyen94] and $\Delta_f H_{298}^\circ(\text{CH}_2\text{NH}_2^+) = +7.72 \pm 0.08$ eV [Holmes2006]

^b Using $\Delta_f H_{298}^\circ(\text{CH}_4) = -0.776 \pm 0.004$ eV [NIST ChemWeb] and $\Delta_f H_{298}^\circ(\text{CH}_3) = +1.510 \pm 0.008$ eV [NIST ChemWeb]

^c Using $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_3) = 3.10 \pm 0.05$ eV and $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_4) = 0.543 \pm 0.005$ eV [NIST ChemWeb]

^d Using $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_4) = 1.970 \pm 0.003$ eV [Argonne Active Thermochemical Table] and $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_3 \text{ propargyl}) = 3.513 \pm 0.041$ eV [NIST ChemWeb]

^e Using $\Delta_f H_{298}^\circ(\text{C}_3\text{H}_6) = 0.210 \pm 0.003$ eV [Argonne Active Thermochemical Table] and assuming that the C_3H_5 allyl radical (CH_2CHCH_2) is produced, for which $\Delta_f H_{298}^\circ = 1.77 \pm 0.03$ eV [NIST ChemWeb]

^f Using $\Delta_f H_{298}^\circ(\text{CH}_3\text{OH}) = -2.12 \pm 0.10$ eV [NIST ChemWeb] and assuming that the CH_3O methoxy radical is produced, for which $\Delta_f H_{298}^\circ = +0.176 \pm 0.041$ eV [NIST ChemWeb]

The CS for reaction (3) as a function of the collision energy are given in **Fig. 8**. The three unsaturated species (C_2H_4 , C_3H_4 and C_3H_6) show a gradual decrease with increasing collision energy, whereas the saturated species (CH_4 and CH_3OH) both show a rise in CS at intermediate collision energies before plateauing at higher collision energies, with this feature being amplified for the HCNH_2^{++} isomer in both cases.

Fig. 8: Reactive cross sections (CSs) as a function of E_{CM} for the reaction of HCNH_2^+ (top) and H_2CNH^+ (bottom) with different R-H neutrals to give CH_2NH_2^+ products (m/z 30). The photon energy used is $E_{phot} = 11.48$ eV in all cases with the exception of HCNH_2^+ plus CH_3OH ($E_{phot} = 12.98$ eV) and HCNH_2^+ plus C_2H_4 ($E_{phot} = 1.98$ eV). Since in these cases the dependence of CS with E_{phot} is flat, such differences have no influence on the CS values as a function of E_{CM} .

The difference between the saturated and unsaturated species can be explained by the ability of the unsaturated species to form covalently-bound adducts, through which the reaction can proceed rapidly and often with little or no barrier. Whereas, for the saturated species, the chemistry at low collision energies is dominated by the formation of van der Waals complexes where there is a competition between dissociation into products and back-dissociations towards the reagents. At higher energies the reaction with saturated hydrocarbons will probably mainly proceed by a stripping mechanism.

The similarities in the CS trends with collision energy for CH_4 and CH_3OH support the hypothesis that they result from the competition between the two different mechanisms: direct H atom transfer and reaction proceeding via formation of an intermediate complex. Since the C-H and O-H bond dissociation enthalpies in CH_4 and CH_3OH are essentially identical (4.555 ± 0.001 and 4.54 ± 0.03 eV respectively [Blanksby03]), reaction enthalpies are not sufficient to explain the larger cross section observed for CH_3OH in the entire collision energy range, which is instead due to the presence of a dipole moment in methanol, thus leading to a more strongly bound adduct with CH_3OH than with CH_4 .

5. Conclusions

Dissociative photoionization experiments of suitable neutral precursors (cyclopropylamine and azetidine) using tuneable VUV photons in the range 10-14 eV and associated calculations confirm the possibility to produce the H_2CNH^{+} and HCNH_2^{+} radical cations independently and selectively. Both isomers react with CH_4 to exclusively give H_2CNH_2^+ plus CH_3^+ . Differences in the reactive cross sections as a function of the collision energy are interpreted, with the aid of theoretical calculations, in terms of competition between direct stripping and complex-mediated H atom transfer. Our study provides the first experimental measure of the absolute cross sections for the reactions of H_2CNH^{+} / HCNH_2^{+} with CH_4 .

Acknowledgements

We are grateful to the DESIRS beamline team for assistance during the synchrotron measurements and the technical staff of SOLEIL for the smooth running of the facility under projects n° 20180118 and 20190249. We thank prof. Marzio Rosi (University of Perugia, IT) for useful discussions on the theoretical calculations. This work was supported by the European Union's Horizon 2020 research and innovation programme "Astro-Chemistry Origins" (ACO), Grant No 811312. W.G. thanks the Swedish Research Council for a project grant (grant number 2019-04332). M.P. and J.Ž. acknowledge support from the Ministry of Education Youth and Sports of the Czech Republic (grant No. LTC20062). V.R. acknowledges funding for a PhD fellowship from the Dept. Physics, University of Trento.

Formatted: Font: (Default) Arial, 11 pt, English (United Kingdom), Check spelling and grammar

Bibliography

- [Alcaraz 2004] C. Alcaraz, C. Nicolas, R. Thissen, J. Žabka, and O. Dutuit, *J. Phys. Chem. A* 108 (2004) 9998–10009 doi: 10.1021/jp0477755
- [Anderson95] Y.-H. Chiu, H. Fu, J.-T. Huang, and S.L. Anderson, *J. Chem. Phys.* 102 (1995) 1199.
- [Anicich 2003]: V. G. Anicich, JPL-Publication-03-19 (2003) <http://hdl.handle.net/2014/7981>
- [ATcT] B. Ruscic, D. H. Bross, Active Thermochemical Tables (ATcT) values based on ver. 1.122e of the Thermochemical Network, Argonne National Laboratory (2019); available at ATcT.anl.gov
- [Audier2003] J. Chamot-Rooke, P. Mourgues, G. van der Rest, H.E. Audier, *Int. J. Mass Spectrom.* 226 (2003) 249–269
- [Baer2000] T. Baer, Y. Song, J. Liu, W. Chen, C. Y. Ng, *Faraday Discuss.* 115 (2000) 137–145
- [Balucani19] C. H. Yuen, M. A. Ayouz, N. Balucani, C. Ceccarelli, I. F. Schneider and V. Kokoouline, *MNRAS* 484 (2019) 659–664
- [Benson1976] Benson S. W. “Thermochemical Kinetics”; Wiley-Interscience: New York, 1976.
- [Blanksby03] S.J.Blanksby, G. B. Ellison, *Acc. Chem. Res.* 36 (2003) 4, 255–263
- [Bohme2009] A. Shayesteh, V. V. Lavrov, G. K. Koyanagi, D. K. Bohme, *J. Phys. Chem. A* 113 (2009) 19, 5602–5611 doi:10.1021/jp900671c
- [Bouchoux1998] G. Bouchoux, C. Alcaraz, O. Dutuit, and M. T. Nguyen, *J. Am. Chem. Soc.* 120 (1998) 152–160
- [Bouchoux2000] G. Bouchoux, B. Gaudin, D. Leblanc, M. Yáñez and O. Mó, *Int. J. Mass Spectrom.* 199 (2000) 59–69
- [Burgers1984] P.C. Burgers, J.L. Holmes and J.K. Terlouw, *J. Am. Chem. Soc.* 106 (1984) 2762
- [Castrovilli2014] 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.* 25 (2014) 351–367
- [Cunha 2015] Cunha de Miranda, B., Romanzin, C., Chefdeville, S., Vuitton, V., Žabka, J., Polášek, M., et al. *J. Phys. Chem. A* 119 (2015) 6082–6098 doi: 10.1021/jp512846v
- [Chupka71] W.A. Chupka, *J. Chem. Phys.* 54 (1971) 1936–1947
- [dePretis2009] G. de Petris, A. Troiani, M. Rosi, G. Angelini, O. Ursini *Chem. Eur. J.* 15 (2009) 4248–4252 DOI: 10.1002/chem.200802581
- [Dietl2013] N. Dietl, A. Troiani, M. Schlangen, O. Ursini, G. Angelini, Y. Apeloig, G. de Petris and H. Schwarz, *Chem. Eur. J.* 19 (2013) 6662–6669 DOI: 10.1002/chem.201204157
- [Eckhardt2018] A. K. Eckhardt and P. R. Schreiner, *Angew. Chem. Int. Ed.* 57 (2018) 5248 – 5252
- [GAUSSIAN] Gaussian 09, Revision D.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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[Holmes1992] J.L. Holmes, F.P. Lossing and P.M. Mayer, *Chem. Phys. Lett.* 198 (1992) 211.

[Holmes2006] Holmes J., Aubry, C., and Mayer, P. *Assigning Structures to Ions in Mass Spectrometry* (2006) CRC Press, Taylor & Francis Group, Boca Raton FL (USA)

[Holzmeier2013] F. Holzmeier, M. Lang, K. Hader, P. Hemberger, and I. Fischer *J. Chem. Phys.* 138 (2013) 214310

[Lavvas2008] P. Lavvas, A. Coustenis, and I. Vardavas *Planet. Space Sci.* 56 (2008) 67

[Mercier 2000] Mercier, B; Compin, M; Prevost, C; et al. *J. Vacuum Sci. Technol. A-VACUUM SURFACES AND FILMS* 18 (2000) 2533-2541 DOI: 10.1116/1.1288196

[Minnhagen 1973] L. Minnhagen, *J. Opt. Soc. Am.* 63 (1973) 1185–1198
DOI:10.1364/JOSA.63.001185

[Nahon 2012] L. Nahon, N. de Oliveira, G.A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde and F. Polack, *J. Synchrotron Rad.* 19 (2012) 508–520. doi: 10.1107/S0909049512010588

[Nguyen1994] M. T. Nguyen, J. Rademakers, J.M.L. Martin, *Chem. Phys. Lett.* 221 (1994) 149

[NIST ASD] NIST Atomic Spectra Database. Available: <http://physics.nist.gov/asd>

[NIST Chem] NIST Chemistry WebBook, NIST Standard Reference Data Base Number 69, Gaithersburg, MD: National Institute of Standards and Technology

[Polce1997] M.J. Polce Y. Kim, C. Wesdemiotis, *Int. J. Mass Spectrom. Ion Proc.* 167/168 (1997) 309-315

[Ryan1995] M. F. Ryan, A. Fiedler, D. Schroeder, H. Schwarz, *J. Am. Chem. Soc.* 117 (1995) 7, 2033–2040 doi: 10.1021/ja00112a017

[Schroder1995] D. Schröder, and H. Schwarz, *Angew. Chem. Int. Ed. Engl.*, 34 (1995) 1973-
doi:10.1002/anie.199519731

[Schwarz2012] N. Dietl, M. Schlangen, and H. Schwarz *Angew. Chem. Int. Ed.* 51 (2012) 5544 – 5555

[Schwarz2015] H. Schwarz, *Chem. Phys. Lett.* 629 (2015) 91–101

[Schwarz2017] H. Schwarz, P. Gonzalez-Navarrete, J.L. Li, M. Schlangen, X.Y. Sun, T. Weiske, S.D. Zhou, *Organometallic* 36 (2017) 8-17 DOI: 10.1021/acs.organomet.6b00372

[Shebanits2016] O. Shebanits, J.-E. Wahlund, N. J. T. Edberg, F. J. Cray, A. Wellbrock, D. J. Andrews, E. Vigren, R. T. Desai, A. J. Coates, K. E. Mandt, and J. H. Waite Jr, *J. Geophys. Res. Space Physics* 121 (2016) 10075–10090.

[Skouteris2015] D. Skouteris, N. Balucani, N. Faginas-Lago, S. Falcinelli, and M. Rosi *A&A* 584 (2015) A76

[Spartan] Spartan; Wavefunction Inc.: 18401 Von In Karman Avenue, Suite 370, Irvine, CA 92612 U.S.A., 1994, www.wavefun.com.

[Sundelin21] D. Sundelin, D. Ascenzi, V. Richardson, C. Alcaraz, M. Polášek, C. Romanzin, R. Thissen, P. Tosi, J. Žabka and W. Geppert submitted to *Chem. Phys. Lett.* (2021)

[Tarasenko1986] N.A. Tarasenko, A.A. Tishenkov, V.G. Zaikin, V.V. Volkova and L.E. Gusef'nikov, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1986) 2397

[Teloy 1974] E. Teloy, D. Gerlich, *Chem. Phys.* 4 (1974) 417 - 427.

[Traeger1981] J. C. Traeger and R. G. McLoughlin, *J. Am. Chem. Soc.* 103 (1981) 3647-3652

[Viggiano2020] B.C. Sweeny, H.Q. Pan, A. Kassem, J.C. Sawyer, S.G. Ard, N.S. Shuman, A.A. Viggiano, S. Brickel, O.T. Unke, M. Upadhyay, M. Meuwly, *Phys. Chem. Chem. Phys.* 22 (2020) 8913-8923. DOI 10.1039/d0cp00668h

[Vuitton2006] V. Vuitton, R. V. Yelle, and V. G. Anicich *Astrophys. J.* 647 (2006) L175

[Vuitton2007] V. Vuitton, R.V. Yelle, M.J. McEwan *Icarus* 191 (2007) 722–742

[Vuitton2019] V. Vuitton, R.V. Yelle, S.J. Klippenstei, S.M. Hörst, P. Lavvas, *Icarus* 324 (2019) 120–197

[Westlake2014]. J.H. Westlake, J.H. Waite, N. Carrasco, M. Richard, T. Cravens, J. Geophys. Res. A119 (2014) 5951–5963

[Zabka00] J. Zabka, O. Dutuit, Z. Dolejšek, J. Polach and Z. Herman Phys. Chem. Chem. Phys. 2 (2000) 781-786

Figure 1

Figure 2

[Click here to access/download;Figure;Fig2.tif](#)

Figure 3

[Click here to access/download;Figure;Fig3_rev_hd.jpg](#)

Figure 5

Figure 7

[Click here to access/download;Figure;Fig 7_rev.jpg](#)

Figure 8