

## SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

**Action number:** Action CM1405 - 42939

**STSM title:** *The photoionization of Methyl Isocyanide, Propynal, and 2 Aminoacetonitrile molecules*

**STSM start and end date:** 15/12/2018 to 15/03/2019

**Grantee name:** Mr Zied Gouid

### PURPOSE OF THE STSM:

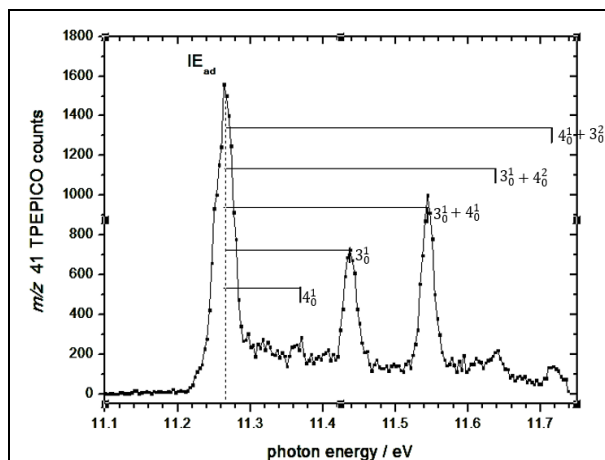
Among all the molecules that could possibly be formed in the interstellar medium (ISM), organic and inorganic cyanide (nitriles) are definitely important molecules. They represent 20% of the approximately 200 molecules detected today in the gas phase of the interstellar medium (ISM). Several of their isomers with the functional group  $-N\equiv C$ , called isonitriles (also isocyanides), are observed in some objects of the ISM.

This research represents a significant step forward towards the understanding of the VUV photophysics of methyl isocyanide  $CH_3NC$  (MIC) which is fully to ISM chemistry. The main aim of this work is to give insight on the stability and reactivity of  $CH_3NC$  under interstellar radiation conditions. The VUV photochemistry of MIC has not been reinvestigated a lot in the past. Here, we present both experimental and theoretical study of the photoionization and the dissociative photoionization of MIC in the gas phase. The experimental part was done by means of a photoelectron/photoion coincidence spectrometer connected to the VUV beamline of the Synchrotron Soleil. The interpretation of the experimental spectra (photoionization mass spectra, TPEPIO and PEPICO spectra) was done with the help of *ab initio* and DFT quantum chemical calculations. These theoretical calculation was based on the determinations of the equilibrium geometry, the adiabatic ionization and the appearance energies of molecules and their fragments and the anharmonic frequencies of  $Mic^+$  cation in the ground state.

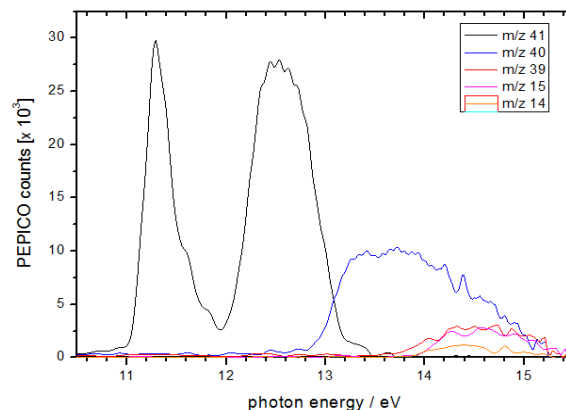
### DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

A combined theoretical and experimental investigation of the single photoionization of gas phase methyl isocyanide (MIC) and its fragmentation pathways has been carried out. MIC was chosen since it is a key compound in astrochemistry and astrobiology. We applied Vacuum Ultraviolet (VUV) synchrotron-based experiments to measure photoelectron photoion coincidence (PEPICO) spectra between 10.6 and 15.5 eV. This technique allowed us to determine the adiabatic ionization energy (AIEs) the fragment ion appearance energies (AE) of MIC. The experimental appearance energies have been attributed to specific dissociation channels with the help of the quantum chemical calculations.

The experimental AIE of MIC has been measured from the TPEPICO spectrum (figure 1). The adiabatic ionization energy of MIC, determined from the center of the first and most intense band (indicated by a vertical dotted line in Fig.1) is found to be  $AIE = (11.263 \pm 0.005)$  eV and is assigned to the  $0_0^0$  origin of the vibronic progression and transition from the neutral ground state to the fundamental state of the cation. This value has never been measured before with such precision. Only a value of  $AIE = 11.24$  eV had been known before (without error bar) from two independent measurements. Furthermore, our value is in excellent agreement the calculated AIE to be  $AIE_{calc} = 11.265$  eV, computed at (R)CCSD(T)-F12 (+CV+SR+ZPVE) level. This value is falls into the precision interval ( $\pm 0.005$  eV) of the experimental AIE.



**Figure 1:** TPEPICO spectra of the methyl isocyanide parent ion ( $m/z$  41). The experimental adiabatic ionization energy (AIE) is taken as the median of the  $0_0^0$  band (indicated by a bar and a vertical dotted line).



**Figure 2.** PEPICO spectra of the  $\text{CH}_3\text{NC}^+$  parent ion and 4 fragment ions seen below 15,5 eV. These spectra are deduced from mass selected PE images by circular integration.

The PEPICO spectra as those reported in Figures 2 show the parent ion  $m/z$  41 and those of the four fragment cations at  $m/z$  40, 39, 15 and 14, respectively in the 10.6-15.5 eV photon energy range.

Two isomeric ions can potentially be formed for the  $m/z$  40 radical cation ( $\text{H}_2\text{C}_2\text{N}^+$ ) corresponding to the H loss reaction from the parent cation (cf. table 1). According to our theoretical results, the pathway  $\text{CH}_3\text{NC}^+ \rightarrow \text{H}_2\text{CCN}^+ + \text{H}$  is energetically lower by 0.6 eV compared to the  $\text{CH}_3\text{NC}^+ \rightarrow \text{H}_2\text{CNC}^+ + \text{H}$  pathway, at (R)CCSD(T)-F12 (+CV+SR+ZPVE) level of theory (cf. Table 1). Furthermore, the calculated appearance energy for  $\text{H}_2\text{CCN}^+$  fragment is  $\text{AE}_{\text{calc}} = 12.881$  eV is in excellent agreement with the experimental appearance energy ( $\text{AE}_{\text{exp}} = (12.8 \pm 0.05)$  eV), being only 30 meV below  $\text{AE}_{\text{calc}}$ . The calculated AE of the  $\text{H}_2\text{CNC}^+$  isomer is  $\text{AE}_{\text{calc}} = 13.499$  eV. We therefore unambiguously assign the observed  $m/z = 40$  fragment cation to the formation of  $\text{H}_2\text{CCN}^+$  by H loss reaction. This means by consequence that  $\text{CH}_3\text{NC}$  isomerizes to  $\text{CH}_3\text{CN}$  during the H loss reaction. The related dynamics remain to be explored.

The experimental appearance energy of  $m/z$  39 is  $\text{AE}_{\text{exp}}(m/z 39) = 13.7 \pm 0.05$  eV, also in excellent agreement with the calculated AE value for the  $\text{CH}_3\text{NC}^+ \rightarrow \text{HCNC}^+ + \text{H}_2$  fragmentation channel. This is confirmed by the present computations as shown in table 1. The calculated AE falls inside the precision interval of the experimental AE determination for this cation. The computed appearance energy for this fragment is  $\text{AE}_{\text{cal}} = 13.708$  eV.

The third observed fragment cation is  $m/z$  15 and associated with the production of a CN radical and  $\text{CH}_3^+$ . We measured its fragment appearance energy to be  $\text{AE}_{\text{exp}}(m/z 15) = 13.9 \pm 0.05$  eV which is close to the calculated  $\text{AE}_{\text{calc}} = 14.050$  eV. The difference between the experimental and theoretical values is  $\sim 0.1$  eV. However, we can confirm the assignment of this energy to the fragmentation pathway  $\text{CH}_3\text{NC}^+ \rightarrow \text{CH}_3^+ + \text{CN}$ .

The experimental appearance energy of  $m/z$  14 is  $\text{AE}_{\text{exp}}(m/z 14) = 13.85 \pm 0.05$  eV, also in excellent agreement with the calculated AE value for the fragmentation pathway corresponding to the loss of neutral HCN:  $\text{CH}_3\text{NC}^+ \rightarrow \text{CH}_2^+ + \text{HCN}$ . Here we calculated  $\text{AE}_{\text{cal}}$  at 13.812 eV for this channel which is inside the precision interval of the experimental AE.

**Table 1:** Calculated and measured appearance energies (AEs) of the different fragmentation pathways of the resulting cation of methyl isocyanide.  $\Delta$ ZPE is evaluated at the PBE0/aVTZ level using the corresponding anharmonic frequencies. The equilibrium structure of these species is given in Table S2 of the supplementary material.

Species	H	H2CNC+	H2CCN+	H2	HCNC+	CN	CH3+	HCN	CH2+
<b>PBE0/ aug-cc-pVDZ (hartree)</b>	-0,50065063	-	-	-1,1638	-130,8844	-92,6120	-39,4220	-93,3212	-38,7199
<b>ZPVE / PBE0/aug-cc-pVDZ (kcal/mol) and (eV)</b>	0 0	19,78955 0.858156328	19.80820 0.858965069	6,2462 0.2708609	10,6962 0.46383125	3,1059 0.1346846	19,5967 0.84979356	9,1835 0.3982344	10,2440 0.444222
<b>CCSD(T)-F12 /cc-VTZ-F12 (hartree)</b>	-0,49999462	-131,53053803	-131.5532977	-1,17380611	-130,84419968	-	-39,41640706	-	-38,70852617
<b>CCSD(T,fc)/cc-pwCVTZ (hartree)</b>	-0.49980981	-131.49395993	-131.49944760	-1.17211990	-130.80941376	-	-39.40604212	-	-38.70027215
<b>CCSD(T,full)/cc-pwCVTZ (hartree)</b>	-0.49980981	-131.64005646	-131.6461163	-1.17211990	-130.9551	-	-39.45360317	-	-38.74744125
<b>CCSD(T)/cc-pVTZ (hartree)</b>	-0,4998098	-131,4856688	-131.4911709	-1,1721199	-130,8017593	-92,5656927	-39,4041902	-93,2751288	-38,6986252
<b>CCSD(T)/cc-pVTZ-DK (hartree)</b>	-0,4998098	-131,4819439	-131.4874734	-1,1721207	-130,7980222	-92,5626965	-39,4033771	-93,2722222	-38,6978056
Appearance energies									
<b>CCSD(T)-F12 /cc-VTZ-F12 (SP) (eV)</b>	13,8872004	13,23754175	14,19772537	14,25740563	14,17033805				
<b>PBE0/ aug-cc-pVDZ (opt) (eV)</b>	13,72349969	13,57624464	14,17155139	14,55794759	14,36474949				
<b>CV (hartree)</b>	0,0011043	0,0005321	0,001514	0,00141468	0,00101977				
<b>(eV)</b>	0,03004910	0,0144789	0,00412110	0,03849485	0,0277489614				
<b>SR (hartree)</b>	-0,0000239	-0,0005321	-0,0000125	-0,0000605	-0,0000226				
<b>(eV)</b>	-0,00065034	-0,00139592	-0,00034013	-0,00164626	-0,00061496				
<b>ZPVE (computed at the anharmonic level using PBE0/AVDZ) (eV)</b>	-0,36984647	-0,369037731	-0,49331065	-0,24352464	-0,3855464				
<b>AE (CCSD(T)-F12 /cc-VTZ-F12 (SP)+CV+SR+ZPVE) (eV)</b>	13,499	12,881	13,708	14,050	13,812				
<b>AE exp (eV) <math>\pm</math> 0.05</b>		12,8	13,7	13,9	13,85				

### DESCRIPTION OF THE MAIN RESULTS OBTAINED

Finally, the most important result of the present study that deserves to be particularly stressed is the very good performance of the composite scheme **(R)CCSD(T)-F12 (+CV+SR+ZPVE)**. This approach, despite the low computational cost, is suitable for providing quantitative predictions close to experimental accuracy in the case of medium-sized molecules of interest in astrophysics.

### FUTURE COLLABORATIONS (if applicable)

This STSM was very fruitful. A solid collaboration between University Tunis El Manar and University Paris-Est Créteil is settled. The results are very encouraging. A common publication will be submitted very soon. This work will be continued on two other astrophysically relevant molecules: 2-Aminoacetonitrile and Methylketene.

