Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Single photon ionization of methyl isocyanide and the subsequent unimolecular decomposition of its cation: experiment and theory

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Table S1: Total energies (in hartree) and calculated and measured adiabatic ionization energies (AIE in eV) of methyl-isocyanide. PBE0 computations correspond to optimization and the other computations are single point computations. CV, SR and ΔZPVE are also given in eV.

Species	MIC	MIC^+
Total energies		
PBE0/aug-cc-pVDZ	-132.5690023	-132.15762236
ZPVE/ PBE0/aug-cc-pVDZ	0.0451282493	0.0452429089
(R)CCSD(T)-F12/cc-VTZ-F12	-132.53976990	-132.12575330
(R)CCSD(T,fc)/cc-pwCVTZ	-132.49749508	-132.08730401
(R)CCSD(T,full)/cc-pwCVTZ	-132.64469585	-132.23451014
(R)CCSD(T)/cc-pVTZ	-132.4889665	-132.0784911
(R)CCSD(T)cc-pVTZ-DK	-132.4852177	-132.0747609
Ionization energies		
IE((R)CCSD(T)-F12/cc-pVTZ-F12)	$E_{CCSD(T)\text{-}F12\ (MIC+)}$-$E_{CCSD(T)\text{-}F12(MIC)}$ =11.265	
CV	$[(E_{M+;(CCSD(T,full)}$-$E_{M;CCSD(T,full)}]$ - $[E_{M+;(CCSD(T,fc))}$-$E_{M;(CCSD(T,fc)}]$ = 0.000146	
SR	$[E_{DKH\text{-}CCSD(T)/cc\text{-}pVTZ\text{-}DK(M+)}$ - $E_{CCSD(T)/cc\text{-}pVTZ(M+)}]$ - $[E_{DKH\text{-}CCSD(T)/cc\text{-}pVTZ\text{-}DK(M)}$-$E_{CCSD(T)/cc\text{-}pVTZ(M)}]$ = 0.00050	
ΔZPVE	$ZPVE_{(M+)}$ - $ZPVE_{(M)}$ = 0.00645	
AIE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +CV+SR+ZPVE (SP))	11.265	
AIE exp	11.263	

Table S2: Total energies (in Hartree) of the different fragmentation pathways of the resulting cation of methyl isocyanide. ZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. The equilibrium structure of these species is given in Table S4 of the supplementary material. PBE0 computations correspond to optimization and the other computations are single point computations.

Species	H	H_2CNC^+	H_2CCN^+	H_2	$HCCN^+$	$HCNC^+$	CN	CH_3^+	HCN	CH_2^+
PBE0/aug-cc-pVDZ	-0.50065063	-131.5640153	-131.569426088	-1.1638	-130.88384252	-130.8844	-92.612	-39.422	-93.3212	-38.7199
ZPVE/PBE0/aug-cc-pVDZ	0	0.858156328	0.858965069	0.2708609	0.4618863036	0.46383125	0.1346846	0.84979356	0.3982344	0.444222
(R)CCSD(T)-F12 /cc-VTZ-F12	-0.49999462	-131.530538	-131.5532977	-1.17380611	-130.83683417	-130.8441997	-92.59940541	-39.41640706	-93.31048602	-38.70852617
(R)CCSD(T,fc)/cc-pwCVTZ	-0.49980981	-131.49395993	-131.49944760	-1.17211990	-130.809934176	-130.80941376	-92.57286514	-39.40604212	-93.28145583	-38.70027215
(R)CCSD(T,full)/cc-pwCVTZ	-0.49980981	-131.64005646	-131.6461163	-1.17211990	-130.95569713	-130.9551	-92.67109021	-39.45360317	-93.38046832	-38.74744125
(R)CCSD(T)/cc-pVTZ	-0.4998098	-131.4856688	-131.4911709	-1.1721199	-130.80115129	-130.8017593	-92.5656927	-39.4041902	-93,2751288	-38.6986252
(R)CCSD(T)/cc-pVTZ-DK	-0.4998098	-131.4819439	-131.4874734	-1.1721207	-130.79745188	-130.7980222	-92.5626965	-39.4033771	-93.2722222	-38.6978056

Table S3: Calculated and measured appearance energies (AEs in eV) of the different fragmentation pathways of the resulting cation of methyl isocyanide. ΔZPE (in eV) is evaluated at the PBE0/aug-cc-pVDZ level using the corresponding anharmonic frequencies. CV and SR are for core-valence and scalar relativistic effects. These AEs are deduced using the total energies of Table S2.

m/z	40		39		15	14
Fragmentation channel	$H + H_2CNC^+$	$H + H_2CCN^+$	$H_2 + HCCN^+$	$H_2 + HCNC^+$	$CN + CH_3^+$	$HCN + CH_2^+$
AE ((R)CCSD(T)-F12 / cc-VTZ-F12 (SP))	13.887	13.237	14.398	14.198	14.257	14.171
AE (PBE0/ aug-cc-pVDZ (opt))	13.723	13.576	14.186	14.171	14.558	14.365
CV	0.030	0.014	0.039	0.004	0.0384	0.027
SR	-0.0006	-0.0014	-0.0013	-0.0003	-0.0016	-0.0006
ZPVE	-0.370	-0.370	-0.495	-0.493	-0.243	-0.385
AE (PBE0/aug-cc-pVDZ (opt) // (R)CCSD(T)-F12 /cc-pVTZ-F12 +CV+SR+ZPVE (SP))	13.499	12.881	13.940	13.708	14.050	13.812
AE exp	12.8 ± 0.05		13.7 ± 0.05		13.9 ± 0.05	13.85 ± 0.05

Table S4: Cartesian coordinates of the methyl-isocyanide, ionized methyl-isocyanide and its fragments as obtained after geometry optimizations at the PBE0/aug-cc-pVDZ level of theory.

CH_3NC				**CH_3NC^+**			
C	0.000000	0.000000	-1.106082	C	0.000000	0.000000	-1.107907
N	0.000000	0.000000	0.30910	N	0.000000	0.000000	0.319344
C	0.000000	0.000000	1.483408	C	0.000000	0.000000	1.454430
H	0.000000	1.032544	-1.475886	H	0.000000	1.039300	-1.438183
H	0.894210	-0.516272	-1.475886	H	0.900060	-0.519650	-1.438183
H	-0.894210	-0.516272	-1.475886	H	-0.900060	-0.519650	-1.438183
H_2CNC^+				**H_2CCN^+**			
C	-0.000680	-1.086909	0.000000	C	1.196489	-0.000035	-0.000015
H	-0.954144	-1.621950	0.000000	H	1.739530	0.944806	0.000035
H	0.952285	-1.622854	0.000000	H	1.739504	-0.944885	0.000035
N	0.000000	0.191355	0.000000	C	-0.186273	0.000107	0.000001
C	0.000990	1.404463	0.000000	N	-1.362904	-0.000050	0.000002
H_2				**$HCNC^+$**			
H	0.000000	0.000000	0.372753	C	-0.172444	-1.107207	0.000000
H	0.000000	0.000000	-0.372753	H	-0.966654	-1.857588	0.000000
				N	0.000000	0.099419	0.000000
				C	0.333553	1.300816	0.000000
CH_3^+				**CN**			
C	0.000000	0.000000	0.000002	C	0.000000	0.000000	-0.624806
H	0.000000	0.946215	0.546262	N	0.000000	0.000000	0.535548
H	0.000000	0.000000	-1.092536				
H	0.000000	-0.946215	0.546262				
CH_2^+				**HCN**			
C	0.000000	0.000000	0.091386	C	0.371799	0.000000	0.293428
H	0.000000	1.035115	-0.274158	N	-0.323845	0.000000	1.203700
H	0.000000	-1.035115	-0.274158	H	1.019294	0.000000	-0.555700

Table S5: PBE0/aug-cc-pVDZ anharmonic frequencies (ν, cm^{-1}) of the normal modes of neutral CH_3NC and the type of vibration.

No.	Symm.	Theo.[a)]	Exp.[b)]	Type of vibration
ν_1	a_1	3071	2966	CH_3 s-stretching
ν_2	a_1	2259	2166	NC stretching
ν_3	a_1	1427	1429	CH_3 s-deformation
ν_4	a_1	989	945	CN stretching
ν_5	e	3163	3014	CH_3 d-stretching
ν_6	e	1461	1467	CH_3 d-deformation
ν_7	e	1130	1129	CH_3 rocking
ν_8	e	275	263	CNC bending

a) This work.

b) Ref. 62.

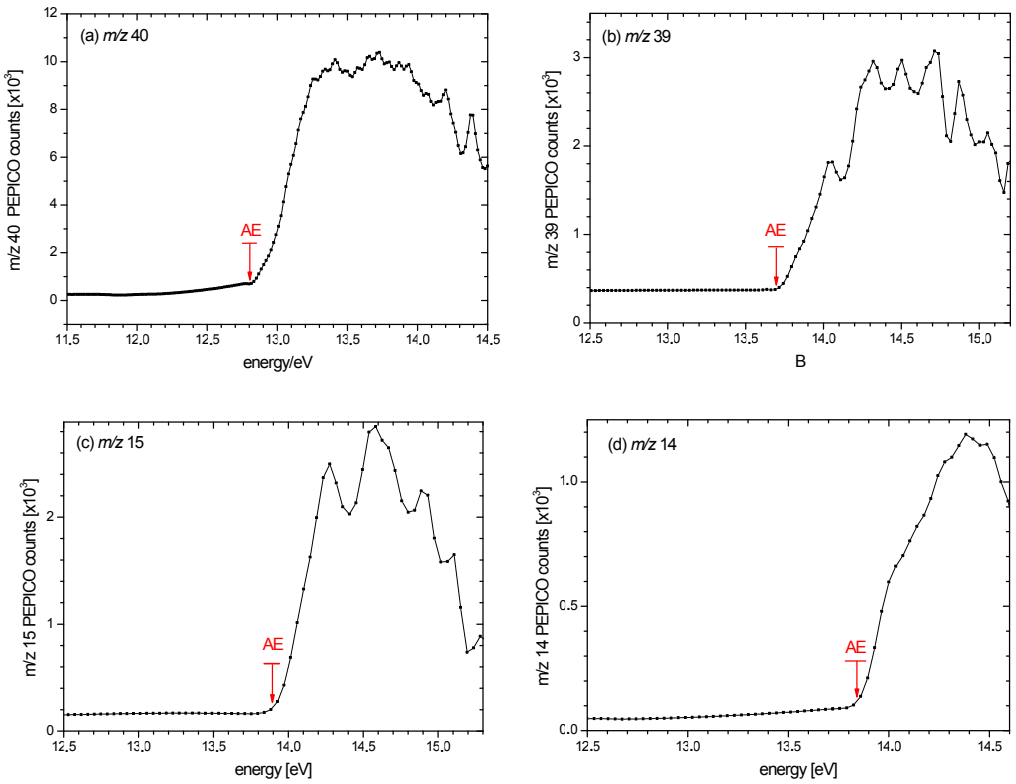

Figure F1 a-d. Experimental appearance energy (AE) determination of the 4 fragmentation pathways observed, as determined from a fixed energy VMI image taken at a photon energy of $h\nu$ = 15.5 eV (same data as figure 3). AEs are indicated as red vertical arrows. In each of the figures F1 a to d, the precision interval is estimated to be ±0.05 eV. They are indicated as a red horizontal bars.