frontiers

Supplementary Material for "Protonation of apolar species: from Cl_2H^+ to (E)-NCCHCHCNH$^+$ through computational investigations"

1 SPECTROSCOPIC CHARACTERIZATION AND GEOMETRICAL PARAMETERS

Table S1. Rotational spectroscopic parameters (MHz, if not otherwise stated) of N_2H^+ and HCO^+ (Watson's S reduction, I^r representation).

Parameter	N_2H^+		HCO^+	
	Theory	Exp.[b]	Theory	Exp.[b]
B_e	46832.71	-	44804.11	-
B_0	46590.46	46586.87549(18)	44565.21	44594.42895(27)
$D_J \times 10^3$	85.4	87.9655(44)	81.1	82.8412(60)
χ(outer)	-5.667	-5.6903(15)	-	-
χ(inner)	-1.336	-1.3582(29)	-	-
μ / D	3.38	-	3.94	-

[a] Equilibrium rotational constants from the "CBS+CV+fT+fQ" approach. Dipole moment components and NQCCs, computed on top of the CBS+CV+fT+fQ reference geometry, at the ae-CCSD(T)/aug-cc-pwCVQZ level. Vibrational corrections to the previous quantities and quartic centrifugal distortion constants at the ae-CCSD(T)/cc-pwCVQZ level of theory. [b] Taken from Cazzoli et al. (2012).

Table S2. Harmonic and anharmonic vibrational frequencies (cm^{-1}) for N_2H^+, and HCO^+. Anharmonic intensities in $km \cdot mol^{-1}$. All quantities are at the ae-CCSD(T)/cc-pwCVQZ level of theory. Experimental vibrational frequencies are also reported.

Mode[a]		Harm. Freq.	Frequency	Intensity	
			N_2H^+		
		Harm. Freq.	Frequency	Intensity	Exp. Freq.[b]
ν_1	Σ	3415.31	3242.08	811.6	3233.96085
ν_2	Σ	2303.32	2265.94	13.1	2257.8667(13)
ν_3	Π	700.94	691.67	231.6	698.6353(14)
			HCO^+		
		Harm. Freq.	Frequency	Intensity	Exp. Freq.[b]
ν_1	Σ	3228.24	3090.31	361.6	3088.7951(31)
ν_2	Σ	2217.56	2187.67	13.0	2183.9496(6)
ν_3	Π	844.02	830.05	75.1	828.2305(9)

[a] The symmetry of the normal mode is given in parentheses. [b] ν_1 taken from Nakanaga et al. (1990), ν_2 taken from Foster and McKellar (1984), and ν_3 from Owrutsky et al. (1986). [c] ν_1 taken from Amano (1983), ν_2 from Kawaguchi et al. (1985), and ν_3 from Foster and McKellar (1984).

Table S3. Vibration-rotation interaction constants (MHz) for N_2H^+, HCO^+, Cl_2H^+, HP_2^+, and HSi_2^+ computed at the ae-CCSD(T)/cc-pwCVQZ level of theory.

Cl_2H^+			
Mode	A	B	C
ν_1	-9704.7429	5.5352	1.0061
ν_2	-121.4252	-45.1464	-44.4238
ν_3	6552.4115	-19.1654	-30.6937
P_2H^+			
Mode	A	B	C
ν_1	-1655.6601	-24.2191	-18.1311
ν_2	1157.0096	-41.9908	-41.3612
ν_3	-15920.7967	-1.8832	-38.5507
Si_2H^+			
Mode	A	B	C
ν_1	2139.1561	-42.4692	-31.6731
ν_2	3150.3941	-54.6221	-52.7126
ν_3	-20058.4973	11.6651	-21.4729
N_2H^+			
Mode		B	
ν_1		-375.6718	
ν_2		-322.9260	
ν_3		216.0976	
HCO^+			
Mode		B	
ν_1		-359.8351	
ν_2		-292.0304	
ν_3		223.1506	

Table S4. Geometrical parameters of N_2H^+, HCO^+, Cl_2H^+, $HP_2{}^+$, and $HSi_2{}^+$ at different levels of theory. Atom labeling according to fig. 1 of the main text. Bond lengths in Angstrom, angles in degrees.

N_2H^+			
Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVQZ	CBS+CV+fT+fQ
R(NN)	1.09919	1.09333	1.09301
R(NH)	1.03466	1.03304	1.03288
HCO^+			
Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVQZ	CBS+CV+fT+fQ
R(CO)	1.11281	1.10614	1.10609
R(HC)	1.09173	1.09230	1.09214
Cl_2H^+			
Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVQZ	CBS+CV+fT+fQ
R(Cl1Cl2)	2.0116	1.99337	1.98573
R(Cl2H)	1.30619	1.30456	1.30561
A(Cl1Cl2H)	98.83	98.98	99.05
$HP_2{}^+$			
Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVQZ	CBS+CV+fT+fQ
R (PH)	1.60318	1.59573	1.59639
A (PPH)	75.24	74.89	74.77
$HSi_2{}^+$			
Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVQZ	CBS+CV+fT+fQ
R(SiH)	1.70495	1.69525	1.69583
A(SiSiH)	83.22	82.82	84.89

Table S5. Geometrical parameters of $NCCH^+$ and $CNNCH^+$ at different levels of theory. Atom labeling according to fig. 1 of the main text. Bond lengths in Angstrom, angles in degrees.

Parameter	fc-CCSD(T)/ jun-cc-PVTZ	ae-CCSD(T) cc-pwCVTZ	CBS+CV
NCCNH+			
R(C1N1)	1.16957	1.16557	1.16283
R(C1C2)	1.37978	1.37650	1.37401
R(C2N2)	1.14621	1.14275	1.14064
R(N2H1)	1.01555	1.01425	1.01350
CNNCH+			
R(C2N2)	1.20434	1.19975	1.19716
R(N2N1)	1.26527	1.26203	1.25967
R(N1C1)	1.14763	1.14425	1.14177
R(C1H1)	1.08129	1.07968	1.07887

Table S6. Geometrical parameters of $NCCHCHCNH^+$ at different levels of theory. Atom labeling according to fig. 1 of the main text. Bond lengths in Angstrom, angles in degrees.

Parameter	CCSD(T)/ jun-cc-PVTZ	rDSD/ jun-cc-pVTZ	CBS+CV
R(C1C2)	1.35432	1.35102	1.34733
R(C1H1)	1.08369	1.08429	1.08158
A(H1C1C2)	124.26	123.90	124.12
R(C2H2)	1.08518	1.08561	1.08294
A(H2C2C1)	121.89	121.74	121.89
R(C1C3)	1.42062	1.41188	1.41314
A(C3C1C2)	119.11	119.61	119.14
R(C3N1)	1.14986	1.14816	1.14371
R(N1H3)	1.00991	1.00956	1.00755
R(C2C4)	1.42807	1.42124	1.42130
A(C4C2C1)	120.84	121.18	120.85
R(C4N2)	1.16592	1.16409	1.15857

2 FORMATION ROUTE

Table S7. Relative energies (with respect to reactants) of the stationary points involved in the formation routes of Cl_2H^+, $HP_2{}^+$, and $CNNCH^+$. The level of theory considered are: revDSD+ZPE, junChS+ZPE and junChS.

$Cl_2 + H_3^+ \rightarrow Cl_2H^+ + H_2$			
Point	revDSD + ZPE	junChS + ZPE	junChS
reac (Ha)	-921.08070	-921.44588	-921.46742
reac	0.00	0.00	0.00
MIN1	-146.23	-143.18	-146.14
TS1	-89.80	-85.72	-91.60
Prod	-129.55	-129.49	-124.38
$P_2 + H_3^+ \rightarrow P_2H^+ + H_2$			
Point	revDSD + ZPE	junChS + ZPE	junChS
reac (Ha)	-683.45241	-683.75986	-683.78187
reac	0.00	0.00	0.00
MIN1	-237.71	-237.74	-233.59
TS2	-165.34	-191.80	-184.26
MIN2	-196.15	-192.42	-187.96
TS1	-46.49	-64.52	-66.25
Prod1	-236.03	-236.13	-226.76
$CNNC + H_3^+ \rightarrow CNNCH^+ + H_2$			
Point	revDSD + ZPE	junChS + ZPE	junChS
reac (Ha)	-186.58339	-186.58339	-186.86554
reac	0.00	0.00	0.00
MIN1	-305.45	-301.23	-309.51
TS1	-5.44	-3.58	-7.20
MIN2	-301.80	-298.88	-305.57
TS2	-32.68	-46.37	-43.52
MIN3	-50.66	-60.62	-65.44
TS3	-301.94	-299.03	-305.58
Prod1	-299.24	-296.02	-298.59
Prod2	-34.50	-47.38	-45.16

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