

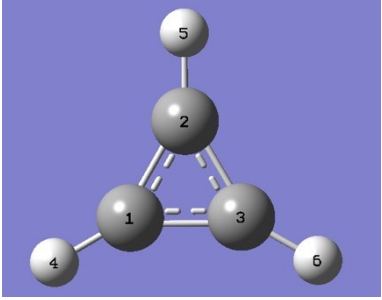
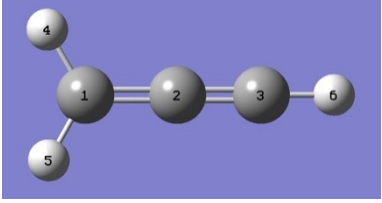
Supplementary information

Valence shell threshold photoelectron spectroscopy of the C_3H_x ($x=0-3$)

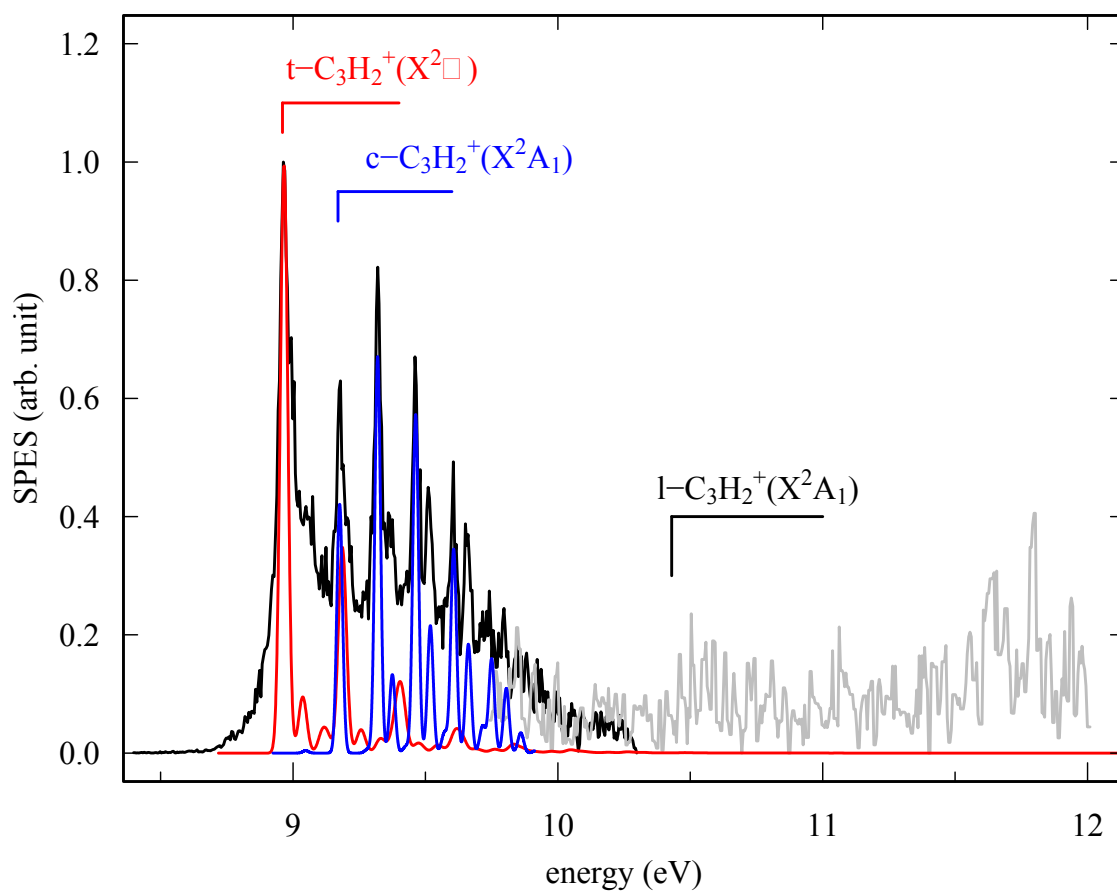
Gustavo A. Garcia^a, Bérenger Gans^b, Julia Krüger^a, Fabian Holzmeier,^{a,c} Anja Röder,^c Allan Lopes,^d Christa Fittschen,^e Christian Alcaraz^d and Jean-Christophe Loison^{f*}

SI1:

Energies at the CCSD(T)-F12/AVQZ (in hartree at 0 K), geometries at the CCSD(T)-F12/AVQZ and frequencies (in cm^{-1} , unscaled) calculated at the at the CCSD(T)-F12/AVTZ level.

Species (Energy, hartree)	Relative energies (kJ/mol)	Geometries	Frequencies (cm^{-1}) ZPE (hartree)
 c- $C_3H_3^+$ (-115.55847522)	0	geometry={ C1; C2,1,B1; C3,2,B2,1,A1; H1,1,B3,2,A2,3,D1; H2,2,B4,1,A3,3,D2; H3,3,B5,2,A4,1,D3} B1 = 1.3626 ANG B2 = 1.3626 ANG B3 = 1.0797 ANG B4 = 1.0797 ANG B5 = 1.0797 ANG A1 = 60.00 DEGREE A2 = 150.00 DEGREE A3 = 150.00 DEGREE A4 = 150.00 DEGREE D1 = 180.00 DEGREE D2 = 180.00 DEGREE D3 = 180.00 DEGREE	761.6, 944.4, 944.4, 1017.0, 1017.0, 1051.9, 1319.0, 1319.0, 1641.3, 3254.4, 3254.4, 3301.2, ZPE = 0.04516528
 l- $C_3H_3^+$ (-115.51154818)	+116	geometry={ C1; C2,1,B1; C3,2,B2,1,A1; H1,1,B3,2,A2,3,D1; H2,1,B4,2,A3,3,D2; H3,3,B5,2,A4,4,D3} B1 = 1.3490 ANG B2 = 1.2305 ANG B3 = 1.0873 ANG B4 = 1.0873 ANG B5 = 1.0742 ANG A1 = 180.00 DEGREE A2 = 120.33 DEGREE A3 = 120.33 DEGREE A4 = 180.00 DEGREE D1 = 6.9234 DEGREE D2 = 186.8545 DEGREE D3 = 45.2693 DEGREE	258.4, 293.9, 629.5, 882.3, 1038.2, 1119.0, 1132.7, 1479.0, 2120.7, 3115.8, 3225.0, 3356.7, ZPE = 0.04249012

SI2:

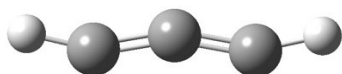


Experimental SPES of C_3H_2 in the 8.5-12 eV range. The curve in grey has been obtained using the $\text{F} + \text{CH}_4$ reaction leading to a smaller production of C_3H_2 .

SI3:

Definition of the HC-C-CH and H-CCC-H angles of Figure 6:

HC-C-CH (CCC "bending"):



H-CCC-H (H-CC "bending"):

