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


**Supporting Information:**

**Table S1:** Cartesian coordinates of the propynal, ionized propynal and its fragments as obtained after geometry optimizations at the PBE0/aug-cc-pVDZ level of theory.

| $C_3H_2O$ ($X\ ^1A'$) | | | | $C_3H_2O^+$ ($X\ ^2A'$) | | | |
|---|---|---|---|---|---|---|---|
| C | 0.729997 | 0.410085 | 0.000021 | C | 0.686708 | 0.412807 | 0.000005 |
| C | -0.679590 | 0.080299 | -0.000351 | C | -0.659815 | 0.084729 | -0.000106 |
| O | 1.615034 | -0.414821 | 0.000084 | O | 1.607703 | -0.416395 | 0.000014 |
| C | -1.874608 | -0.129785 | -0.000160 | C | -1.858185 | -0.131589 | 0.000071 |
| H | 0.949582 | 1.499382 | 0.000569 | H | 1.045273 | 1.472504 | 0.000091 |
| H | -2.924645 | -0.344417 | 0.001691 | H | -2.919146 | -0.337020 | -0.000027 |
| $C_3HO^+$($X\ ^1\Sigma^+$) | | | | $C_3HO^+$($X^1A'$) | | | |
| C | 0.667606 | -0.000814 | -0.000024 | C | 1.800151 | -0.007162 | 0.000015 |
| C | -0.672830 | -0.002351 | 0.000081 | C | 0.457633 | 0.126240 | -0.000028 |
| O | 1.794736 | 0.001140 | 0.000012 | C | -0.835827 | 0.574081 | 0.000005 |
| C | -1.891847 | 0.001043 | -0.000161 | O | -0.867037 | -0.690832 | 0.000004 |
| H | -2.975460 | 0.003614 | 0.000529 | H | -1.595448 | 1.367702 | 0.000019 |
| $C_2H_2^+$($X\ ^2\Pi$) Alcyne | | | | $HC_2^+$($X\ ^1\Sigma^+$) | | | |
| C | 0.000000 | 0.000000 | 0.627057 | C | 0.000000 | 0.000000 | -0.735540 |
| C | 0.000000 | 0.000000 | -0.627057 | C | 0.000000 | 0.000000 | 0.477089 |
| H | 0.000000 | 0.000000 | 1.716176 | H | 0.000000 | 0.000000 | 1.550709 |
| H | 0.000000 | 0.000000 | -1.716176 | | | | |
| $C_2H_2^+$($X\ ^2A_1$) Vinyl | | | | $HCO^+$($X\ ^1\Sigma^+$) | | | |
| C | -0.804631 | -0.000006 | -0.000001 | C | 0.000086 | 0.513989 | 0.000000 |
| C | 0.469826 | -0.000001 | 0.000003 | O | 0.000086 | -0.582491 | 0.000000 |
| H | 1.004380 | 0.973610 | -0.000005 | H | -0.001197 | 1.575994 | 0.000000 |
| H | 1.004452 | -0.973569 | -0.000005 | | | | |
| $CO^{+\circ}$($X\ ^2\Sigma^+$) | | | | | | | |
| C | 0.000000 | 0.000000 | -0.636617 | | | | |
| O | 0.000000 | 0.000000 | 0.477463 | | | | |