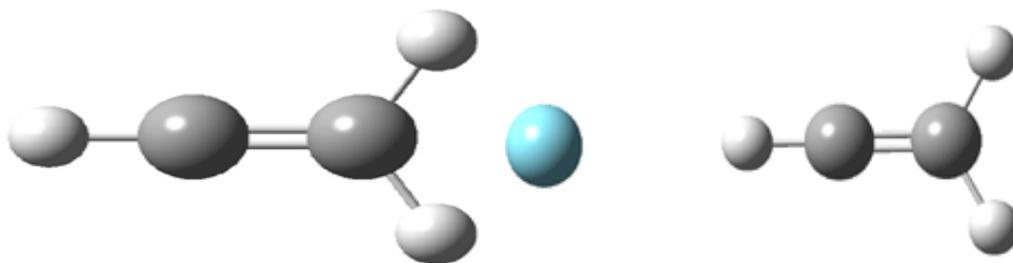
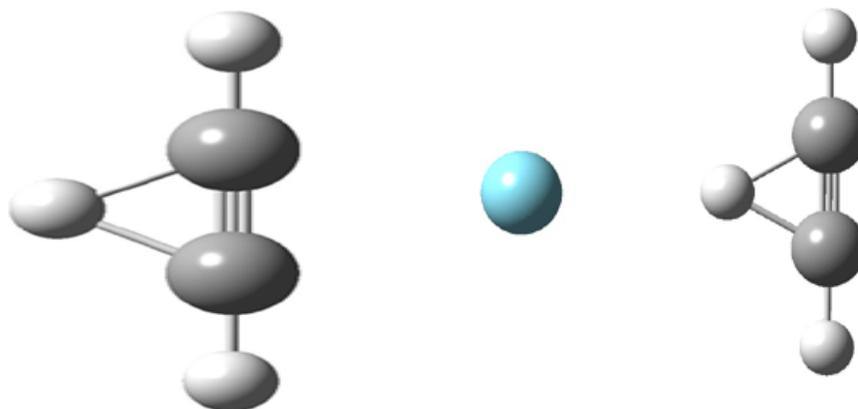


# PROTONATED ACETYLENE

Duncan and Schleyer<sup>1</sup> have investigated protonated acetylene and the protonated acetylene dimer. These ions are created in a pulsed supersonic nozzle/pulsed electrical discharge with a weakly bound argon atom as a tag. IR laser photodissociation spectroscopy allows for the detection of peaks down to 2000  $\text{cm}^{-1}$ , a region not previously explored for this cation. The experimental IR spectrum for  $\text{H}^+(\text{C}_2\text{H}_2)\cdot\text{Ar}$  has two main features: at 3146 and 2217  $\text{cm}^{-1}$ . The 3146  $\text{cm}^{-1}$  corresponds to the previously observed peak<sup>2</sup> at 3142  $\text{cm}^{-1}$  and is similar to the absorption in acetylene (3136  $\text{cm}^{-1}$ ). MP2/6-311+G(2d,2p) computations were performed on the classical and non-classical structures of  $\text{H}^+(\text{C}_2\text{H}_2)$ , with and without a complexed argon atom. These geometries are displayed in Figure 1 and the predicted vibrational frequencies are listed in Table 1.





**Figure 1.** MP2/6-311+<="" p="">

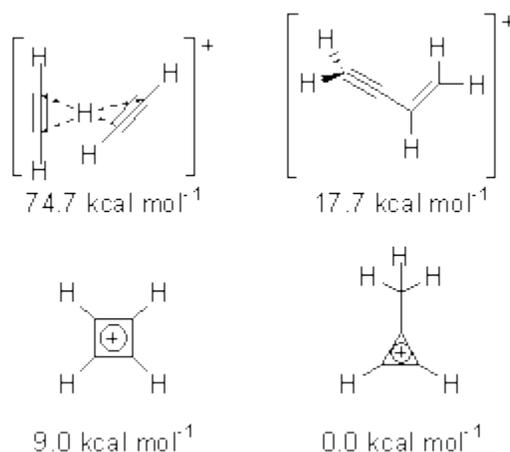
**Table 1.** Relative energies (kcal mol<sup>-1</sup>) and frequencies of protonated acetylene and the protonated acetylene-argon cluster.<sup>1</sup>

	Rel E	Frequencies (scaled)
H <sup>+</sup> (acetylene)Ar non-classical	0.0	3139, 2123
H <sup>+</sup> (acetylene)Ar classical	7.8	3084, 2954, 2878, 1673
H <sup>+</sup> (acetylene) non-classical	0.0	3219, 2250
H <sup>+</sup> (acetylene) classical	7.1	3162, 29947, 2874
Experiment		3364, 3212, 3146, 2217

The argon tag only slightly perturbs the spectrum, as expected for a weakly bond atom remote from most of the hydrogen atoms. The predicted spectra of the two non-classical ions are in nice agreement with the experiment – particularly the interesting peak at 2123 cm<sup>-1</sup> that is due to the bridged proton. This spectra, and the

confirmation of the bridging, non-classical structure, makes a nice pair with the recently reported bridging, non-classical structure of the ethyl cation,<sup>3</sup> which I blogged on previously.

The spectrum of the  $\text{H}^+(\text{C}_4\text{H}_4)$  ion show a doublet at 3129 and 3158  $\text{cm}^{-1}$  and two small peaks at 1261 and 1365  $\text{cm}^{-1}$ . The computed structure that comes closest to matching this spectrum is for the asymmetrically bridged dimer (See Figure 2), though is much more energetic than its isomers. The authors speculate that the bridged dimer is trapped in an energy-well during the thermal expansion, which prevents the formation of the lower energy isomers.



**Figure 2.** Schematic drawing and relative energies of the  $\text{H}^+(\text{C}_4\text{H}_4)$  ion.

Source: <http://comporgchem.com/blog/?p=67>