

## Density Functional Study on Polyacetylene Cations

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Polyacetylenes and their derivatives have been under investigation due to the abundance in combustion and interstellar environments. Cyanopolyacetylenes<sup>1-3</sup> are one of the largest molecules having astrophysical importance, and  $H(C\equiv C)_n$ , CN up to  $n=5$  have been detected in interstellar medium. Intensive studies are being undertaken to characterize these molecules and to elucidate the mechanism of formation of such large molecules in circumstellar environments. Along with neutral polyacetylenes, spectroscopic studies on the corresponding cations have also been carried out as a typical example of open-shell polyatomic cations. Bondybey and co-workers<sup>4,5</sup> and Maier and co-workers<sup>6,7</sup> carried out extensive investigations on these molecules by observing absorption and emission spectra of gas phase and rare gas matrix-isolated cations, and vibrational frequencies in ground or excited electronic states were observed. However, informations on the structures of these cations are still very scarce.

Recently, the density functional theory<sup>8,9</sup> is beginning to find applications to a variety of interesting chemical systems and proves very promising as an alternative to *ab initio* methods. The technique looks very cost effective with accuracy comparable to high level *ab initio* methods. One of the objectives of the present work is to estimate the accuracy of the density functional theory for molecules (open-shell cations) that are usually regarded as cumbersome when treated by *ab initio* methods. In this report, we present density functional calculations on polyacetylene cations  $H(C\equiv C)_nH^+$  ( $n=1-3$ ). Total energies and rotational constants were calculated along with bond lengths, vibrational frequencies and intensities. The expected values of the spin angular momentum  $\langle S^2 \rangle$  were also computed to check spin contamination. Comparisons are made with experimentally observed frequencies and structures. All the calculations were carried out using the GAUSSIAN 94 set of programs<sup>10</sup> on DEC 3000/400 work station.

Table 1 presents the calculated total energies at optimized structures,  $\langle S^2 \rangle$  and rotational constants of the polyacetylene cations  $C_4H_2^+$  and  $C_6H_2^+$  obtained by unrestricted BLYP/6-311G\*\*<sup>11,12</sup> and B3LYP/6-311G\*\*<sup>13</sup> methods. Both of the cations are found to be *linear*. The optimized structures are confirmed by the fact that all the calculated vibrational frequencies are real. It can be seen that there is a small degree of spin contamination for both of the cations. The B3LYP/6-311G\*\* method gives the rotational constant for  $C_4H_2^+$  which is in better agreements with experimental observations by Maier and co-workers<sup>6</sup> than that calculated by the BLYP/6-311G\*\* method. The energies calculated by the B3LYP/6-311G\*\* method are lower than those obtained by BLYP/6-311G\*\* method by 0.04-0.054 Hartree. Table 2 lists the bond

**Table 1.** BLYP/6-311G\*\* and B3LYP/6-311G\*\* energy (a.u.),  $\langle S^2 \rangle$  and rotational constant B (GHz) for  $H-C\equiv C-H^+$ ,  $H-(C\equiv C)_2-H^+$  and  $H-(C\equiv C)_3-H^+$

Molecule	Energy	$\langle S^2 \rangle$	B
$H-C\equiv C-H^+{}^a$	-76.9148656	0.7516	32.8143571
$H-C\equiv C-H^+{}^b$	-76.9416374	0.7517	33.3254342
$H-(C\equiv C)_2-H^+{}^a$	-153.1271092	0.7557	4.357470
$H-(C\equiv C)_2-H^+{}^b$	-153.1668468	0.7570	4.4135054
$H-(C\equiv C)_2-H^+{}^c$	-	-	4.4035921
$H-(C\equiv C)_3-H^+{}^a$	-229.3177404	0.7566	1.3232830
$H-(C\equiv C)_3-H^+{}^b$	-229.3719594	0.7718	1.3392056

<sup>a</sup>BLYP/6-311G\*\*. <sup>b</sup>B3LYP/6-311G\*\*. <sup>c</sup>experimental, Ref. 6.

**Table 2.** The structure of  $H-C\equiv C-H^+$ ,  $H-(C\equiv C)_2-H^+$ , and  $H-C_1\equiv C_2-C_3\equiv C_4-C_5\equiv C_6-H^+$  (bond distances in Å)

	Experimental <sup>a</sup>	BLYP/6-311G**	B3LYP/6-311G**
<b><math>H-C\equiv C-H^+</math></b>			
r(C-H)		1.0861	1.0804
r(C≡C)		1.2568	1.2461
<b><math>H-(C\equiv C)_2-H^+</math></b>			
r(C-H)	1.046	1.0789	1.0736
r(C≡C)	1.234	1.2425	1.2320
r(C-C)	1.346	1.3309	1.3261
<b><math>H-(C\equiv C)_3-H^+</math></b>			
r(C <sub>1</sub> -H)		1.0759	1.0707
r(C <sub>1</sub> ≡C <sub>2</sub> )		1.2366	1.2252
r(C <sub>2</sub> -C <sub>3</sub> )		1.3266	1.3235
r(C <sub>3</sub> ≡C <sub>4</sub> )		1.2535	1.2421

<sup>a</sup>Ref. 6

lengths of  $C_4H_2^+$  and  $C_6H_2^+$ . The C≡C and C-C bond lengths for the  $C_4H_2^+$  cation agree with experimental results very well, while the C-H distance shows difference of about 0.03 Å. Structure of  $C_6H_2^+$  has not been determined experimentally yet, and only the calculated bond lengths are given in Table 2. The bond lengths calculated by the BLYP/6-311G\*\* and B3LYP/6-311G\*\* methods are very similar to each other. The calculated vibrational frequencies (BLYP/6-311G\*\*) are reported in Table 3 along with the experimentally observed frequencies. Very good agreements are noticed between the calculated frequencies for carbon-carbon stretching modes and the experimental ones, typical differences being smaller than 20 cm<sup>-1</sup>. However, large differences between the calculated and observed frequencies are observed for the modes involving C-H stretching. We also experienced similar difficulties for C-H stretching frequencies in other carbon clusters doped with heteroatoms (O, N, S).<sup>14</sup> The frequencies for the symmetric and antisymmetric C-H stretching modes are found to be very close to each other for both of the cations. The origin of the disagreement between the calculated (932 cm<sup>-1</sup>) and the experimentally observed (865 cm<sup>-1</sup>) frequency is not clear. Since the density functional theory calculations are known<sup>15</sup> to yield inaccurate frequencies for the bending modes of the linear molecules with

**Table 3.** Stretching frequencies ( $\text{cm}^{-1}$ ) and relative intensities for  $\text{H}-(\text{C}\equiv\text{C})_2\text{-H}^+$  and  $\text{H}-(\text{C}\equiv\text{C})_3\text{-H}^+$ 

$\text{H}-(\text{C}\equiv\text{C})_2\text{-H}^+$		$\text{H}-(\text{C}\equiv\text{C})_3\text{-H}^+$	
exp. <sup>a</sup>	calc. <sup>b</sup>	exp.	calc. <sup>b</sup>
3143 (s C-H)	3306 (0) $\sigma_g$		3331 (0) $\sigma_g$
	3302 (384) $\sigma_u$		3329 (396) $\sigma_u$
2177(s C=C)	2171 (0) $\sigma_g$	2181.4 <sup>c</sup> , 2182 <sup>d</sup> (s C=C)	2177 (0) $\sigma_g$
	1860 (220) $\sigma_u$		2061 (531) $\sigma_u$
865 (s C-C)	932 (0) $\sigma_g$	1903.4 <sup>c</sup> , 1903 <sup>d</sup> (s C=C)	1915 (0) $\sigma_g$
			1237 (7) $\sigma_u$
		635 <sup>c</sup> , 632 <sup>d</sup> (s C-C)	641 (0) $\sigma_g$

<sup>a</sup>Ref. 4. <sup>b</sup>BLYP/6-311G\*\*. <sup>c</sup>neon-matrix, Ref 5. <sup>d</sup>gas phase, Ref. 7

**Table 4.** Calculated stretching frequencies ( $\text{cm}^{-1}$ ) and relative intensities for  $\text{H-C}\equiv\text{C-H}^+$ 

BLYP/6-311G**	B3LYP/6-311G**	Symmetry
3288 (0)	3360 (0)	$\sigma_g$
3191 (404)	3258 (450)	$\sigma_u$
1823 (0)	1888 (0)	$\sigma_g$

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doublet electronic states, they are not listed in this report. We also find that the B3LYP/6-311G\*\* method give poorer stretching frequencies than the BLYP/6-311G\*\* method, while yielding better structures. Table 1, Table 2 and Table 4 include similar results for  $\text{C}_2\text{H}_2^+$  cation. Although no experimental results are available for comparison, we include the calculated results for the  $\text{C}_2\text{H}_2^+$  cation for completeness. Experimental studies on the structures of this cation by techniques such as the Fourier transform microwave spectroscopy as done by Endo and coworkers,<sup>16-18</sup> would be highly desirable.

Good agreements of the calculated structures and the vibrational frequencies presented in this paper with the experimentally measured values indicate great usefulness of the density functional theory for treating these open shell cations, although we found that the theoretical methods give poor results for frequencies of the C-H stretching modes. Typically the calculated frequencies are larger than the observed values by about  $100 \text{ cm}^{-1}$ . Even though the absolute values of the calculated frequencies may differ from the experimental ones for C-H stretching modes, however, there exists very little confusion over assigning them, since it

is usually the mode with the highest frequency. Theoretical studies on other carbon clusters mixed with hetero atoms are in progress. We hope that our calculations will stimulate further experiments on these very interesting molecules.

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