

# Vibrational-Rotational Spectra of Normal Acetylene and Doubly Deuterated Acetylene: Experimental and Computational Studies

C. ANDREW<sup>1</sup>, E. E. ETIM<sup>1\*</sup>, O. A. USHIE<sup>1</sup> and G. P. KHANAL<sup>2</sup>

<sup>1</sup>Department of Chemical Sciences, Federal University Wukari, PMB 1020 Wukari, Taraba State, Nigeria

<sup>2</sup>Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

*emmaetim@gmail.com*

Received 18 July 2017 / Accepted 12 September 2017

**Abstract:** Two molecules of astrophysical interest, normal acetylene ( $C_2H_2$ ) and deuterated acetylene ( $C_2D_2$ ) were synthesized and their spectra have been recorded using Fourier Transform Interferometer (FTIR) at low resolution between 400 and 4000  $cm^{-1}$ . Vibrational bands and frequencies of interest have been identified and analyzed. Experimental excited rotational constants (B) and ground rotational constant (B) respectively for  $C_2H_2$  as  $35.4172 \pm 0.0036$  and  $35.3348 \pm 0.036$  GHz while for  $C_2D_2$  as  $25.3820 \pm 0.0045$  and  $25.2771 \pm 0.0045$  GHz have been determined. At the MP2 level of theory with the aug-cc-pvtz basis set, we calculated the equilibrium rotational constant of  $C_2H_2$  to be 35.1819 GHz and 25.2495 GHz for  $C_2D_2$ . While, at CCSD(T) level of theory with the same basis set, rotational constant value of 35.0892 and 25.2574 GHz were calculated for  $C_2H_2$  and  $C_2D_2$  respectively. The experimental C-H and C-C bond lengths of acetylene were calculated to be 1.08653 Å and 1.18983 Å respectively. The importance and the astrophysical relevance of these results are discussed.

**Keywords:** Acetylene, Spectra, Experimental, Computational

## Introduction

The molecular species astronomically observed in the thin space between the stars interstellar molecular species play significant roles in diverse fields of study such as atmospheric chemistry, astrochemistry, prebiotic chemistry, astrophysics, astronomy, astrobiology, *etc* and in our understanding of the solar system the world around us. With the collaboration between the spectroscopists and the astrophysicists initiated with the purpose of assigning the Fraunhofer lines in the solar spectrum to atomic transitions in the 18<sup>th</sup> century over 200 different molecular species in the interstellar medium (ISM). These molecular species range from the simple diatomics like hydrogen molecular, carbon monoxide, *etc.*, to the complex molecular species (those with six atoms and above) up to those the

bulky balls like the C<sub>60</sub>, C<sub>70</sub>, *etc.*, with each of these molecular species telling us the story of the chemistry and physics of the environment from which they were detected<sup>1-8</sup>.

Acetylene, (C<sub>2</sub>H<sub>2</sub>)- a known interstellar molecular species is an important organic compound belonging to the alkyne family. The molecule however, has a more fundamental role in science than just been an organic compound. Its application cuts across different areas of sciences including contribution in the development of high-resolution spectroscopy, intra-molecular dynamics, astrochemistry, metrology, intermolecular collision and spectral intensity<sup>9</sup>.

Spectroscopy has been an indispensable tool to scientists in determining the structure of molecules. The infra-red spectroscopy has been widely utilized for probing the vibrational and rotational energy levels of molecules by chemists for structural elucidations. The vibrational-rotational spectra of acetylene molecule both in the ground electronic and excited states in the last decades were extensively investigated using spectroscopic methods<sup>10-12</sup>. The annex 1 of Herman *et al.*,<sup>10</sup> provides an abundant reference of most literature papers of the spectroscopic data on acetylene in the ground electronic state. Been a symmetric linear molecule with D<sub>∞h</sub> point group symmetry, acetylene in its ground state have seven vibrational normal modes with two being doubly degenerate thus giving rise to five distinct fundamental frequencies. The conventional labeling is ν<sub>1</sub> and ν<sub>3</sub> for the symmetric and asymmetric C-H stretches respectively, ν<sub>2</sub> for the C-C stretching vibration, ν<sub>4</sub> (trans) and ν<sub>5</sub> (cis) for the degenerate bends. The ν<sub>3</sub> asymmetric stretch and the doubly degenerate ν<sub>5</sub> cis-bend produces an oscillating change in zero-dipole moment of the molecule and have been experimentally determined to be infrared active<sup>13</sup>. The IR inactive modes include the ν<sub>1</sub> symmetric stretch, the ν<sub>2</sub> C-C stretch and the doubly degenerate ν<sub>4</sub> trans-bend. However, other non-fundamental bands often appear in the infrared spectra of acetylene and are term combination bands which have also been a subject of investigation and the results are widely reported in the literature<sup>11,14</sup>

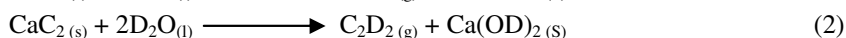
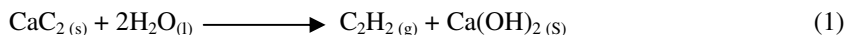
Several spectroscopic techniques have been applied to record the vibration-rotation spectra of acetylene. For instance, Keppler *et al.*,<sup>15</sup> used spectrograph recordings, spectro to analyzed the vibrational spectra of acetylene while Kostyk and Welsh<sup>16</sup> and Bermejo *et al.*,<sup>17</sup> have used conventional and stimulated Raman spectroscopy respectively for this purpose. Depending on the availability of techniques, others studies used Fourier transform interferometers (FTIR)<sup>8</sup> sometimes with synchrotron radiation<sup>19</sup> or femtosecond laser<sup>20</sup> absorption sources to probe the vibrational excited acetylene. Laser techniques such as optoacoustic laser (OAS)<sup>21</sup>, continuous-wave cavity ring down (CWCRDS)<sup>22</sup> and intra-cavity laser absorption (ICLAS)<sup>23</sup> spectroscopies were equally utilized by other authors for the analysis of spectra of acetylene.

In this study, normal acetylene (C<sub>2</sub>H<sub>2</sub>) and deuterated acetylene (C<sub>2</sub>D<sub>2</sub>) were synthesized and standard spectroscopic method namely Fourier transform interferometer, FTIR have been used for structural elucidation. Spectra of the two molecules were recorded at medium resolution (0.5 cm<sup>-1</sup>) and analyzed to determine rotational constants, C-H and C-C bond lengths. We have further used computational methods to determine some of these parameters with the view to compare it with experimental results.

## Experimental

Acetylene (C<sub>2</sub>H<sub>2</sub>) and deuterated acetylene (C<sub>2</sub>D<sub>2</sub>) were synthesized through one step reactions (Equations 1 and 2) contained in a vacuum line. About 2.5 g of calcium carbide (CaC<sub>2</sub>) was weighed and placed in a flask to which distilled water (3 mL) was added through the rubber septum using a syringe to produced C<sub>2</sub>H<sub>2</sub> gas. The acetylene gas synthesized during the reaction was then filled into an IR cell through the vacuum line to a pressure of

about 300 Torr. Same procedure was used to synthesize  $C_2D_2$  except deuterium oxide ( $D_2O$ ) was used instead of  $H_2O$ .



### Spectroscopy measurement

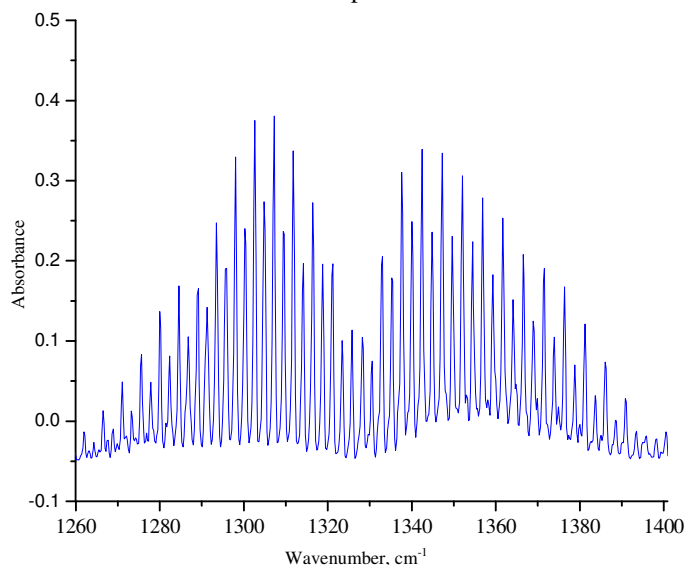
Using Shimadzu FT-IR spectrometer model 21, the spectra of the synthesized  $C_2H_2$  and  $C_2D_2$  were recorded in the region of  $400-4000\text{ cm}^{-1}$ .

### Computational method

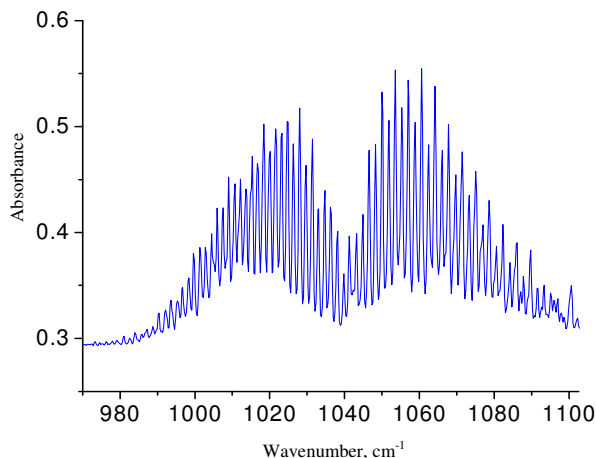
All quantum chemical calculations were carried out using Gaussian 09. Methods of Frisch *et al.*,<sup>24</sup> was adopted and the geometry of the two molecules (normal acetylene and deuterated acetylene) was optimized at two different levels of theories. The second order Møller-Plesset (MP2) and couple cluster including single, double, and linearized triple excitations CCSD(T) level of theory with Dunning's correlation consistent augmented triple- $\zeta$  basis set (Aug-cc-pVTZ) were used for all computations. Harmonic vibrational frequencies were calculated at the same level of theories to confirm the structures are true minima on the singlet potential energy hyper-surface chosen for all of the calculations. Parameters of interest were then obtained from the output file after a successful optimization of the structures.

## Results and Discussion

Figures 1 and 2 shows the  $\nu_4 + \nu_5$  parallel combination bands spectra of  $C_2H_2$  and  $C_2D_2$  respectively recorded at low pressure. From this spectra, the first ten line transition frequencies of P and R branches of  $C_2H_2$  and  $C_2D_2$  were identified and the bands analyzed to determine the rotational constant in the ground ( $B''$ ) and excited ( $B'$ ) electronic states. From the calculated rotational constants, accurate values of moment of inertia, C-H and C-C bond lengths were then obtained and the results are presented in Table 1.



**Figure 1.** Portion of FTIR spectrum of  $C_2H_2$  in the region of  $\nu_4 + \nu_5$  showing P and R branches



**Figure 2.** FTIR spectrum of  $C_2D_2$  in the region of  $\nu_4 + \nu_5$  showing P and R branches

In Table 1, the experimental and calculated results of rotational constants and bond lengths are reported. The difference between the experimental and calculated results was determined to know the extent of deviation. From our results, the extent of equilibrium rotational constant deviation was higher (24.56%) using CCSD(T) calculations than using MP2 (15.29%) for normal acetylene. However, CCSD(T) and MP2 calculations for equilibrium rotational constants for deuterated acetylene gave a small deviation of 1.97% and 2.76% respectively.

**Table 1.** Rotational constants and bond length of  $C_2H_2$  and  $C_2D_2$

Molecule	Parameter	Experimental	Calculated (equilibrium values)	
			MP2	CCSD(T)
$C_2H_2$	$B'' \pm \sigma$ (GHz)	$35.3348 \pm 0.0366$	35.1819	35.0892
	$B' \pm \sigma$ (GHz)	$35.4172 \pm 0.0036$	-	-
	$r_{C-H}$ (Å)	$1.08653 \pm 0.0057$	1.0609	1.0640
	$r_{C-C}$ (Å)	$1.18983 \pm 0.0010$	1.2092	1.2102
$C_2D_2$	$B'' \pm \sigma$ (GHz)	$25.2771 \pm 0.0045$	25.2495	25.2574
	$B' \pm \sigma$ (GHz)	$25.3820 \pm 0.0045$	-	-
	$r_{C-H}$ (Å)	-	1.0612	1.06395
	$r_{C-C}$ (Å)	-	1.2122	1.2102

From the experimental results, there are excellent agreements of the bond length of normal acetylene with previous literature studies. For instance, in recent research by Herman *et al.*,<sup>11</sup> bond length of C-H and C-C in  $C_2H_2$  have been reported as 105.756(52) pm and 120.830(20) pm respectively. While in this study we found the C-H and C-C bond length as  $1.08653 \pm 0.0057$  Å and  $1.18983 \pm 0.0010$  Å respectively. The optimization of the geometry of acetylene using CCSD(T) gave C-H and C-C bond lengths of 1.06 and 1.2 Å respectively which are very satisfactory in agreement with experimental data. From Table 1, the experimental and theoretical rotational constants agree well. The ground state rotational constant of  $C_2H_2$  was studied by Robert *et al.*,<sup>25</sup> and found a value of  $1.1766461$  (1)  $cm^{-1}$  while that of  $C_2D_2$  was reported to be  $0.817872(4560)$   $cm^{-1}$  by Cane *et al.*,<sup>14</sup>

Table 2 compares the experimental vibrational frequencies and that from quantum chemical calculations. The value of the experimental frequencies for normal and deuterated

acetylene agrees well with that from both the theories used. However, other vibrational frequencies were overestimated by the level of theory used.

**Table 2.** Vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{D}_2$

		$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$
$\text{C}_2\text{H}_2$	Experimental	3371.65	1974.30	3294.80	598.62	729.55
	MP2	3534.52	1974.95	3447.12	610.29	747.28
	CCSD(T)	3502.83	1995.44	3394.90	593.31	593.31
$\text{C}_2\text{D}_2$	Experimental	2704.32	1,766.48	2,431.33	504.03	538.12
	MP2	2792.23	1763.85	2523.35	499.03	551.02
	CCSD(T)	2780.57	1778.19	2492.57	494.57	549.61

Force constants in a molecule describe the strength of bonds in the molecule. Using the vibrational frequencies of normal and deuterated acetylene, the force constants were determined and the results shown in Table 3. The result agrees satisfactorily with literature values.

**Table 3.** Bending and stretching force constants for normal and deuterated acetylene.

	$k_s/\text{N m}$	$k_{\delta\delta}/\text{N m}$	$k_r/\text{N m}^{-1}$	$k_{rr}/\text{N m}^{-1}$	$k_{rR}/\text{N m}^{-1}$	$k_R/\text{N m}^{-1}$
$\text{C}_2\text{H}_2$	$2.4733 \times 10^{-19}$	$9.6926 \times 10^{-20}$	584.5961	-10.1712	-3.5305	1684.8891
Lit. <sup>26</sup>	$2.3913 \times 10^{-19}$	$8.7777 \times 10^{-20}$	572	-	-3.7	1572
$\text{C}_2\text{D}_2$	$2.8436 \times 10^{-19}$	$1.3224 \times 10^{-19}$	587.5851	-13.1602	-11.6782	1668.5938

## Conclusion

In this study, we have investigated the structures of normal and deuterated acetylene using experimental (FT-IR) and quantum chemical methods. FTIR was used to obtain the spectra of the molecules. Infrared regions of interest were analyzed and several vibrational bands were observed and assigned with frequency. Rotational constants (ground and excited states), force constants and bond lengths of normal and deuterated acetylene were calculated and the results obtained are in good agreement with previous studies. Results from the quantum chemical calculations obtained indicate that it can be used to know the extent of the exact experimental results.

## References

1. Etim E E and Arunan E, *Planex News letter*, 2015, **5(2)**, 16-21.
2. Emmanuel E. Etim, Prsanta Gorai, Ankan Das, Sandip Charabati and Arunan E, *The Astrophys J.*, 2016, **832(2)**, 144; DOI:10.3847/0004-637X/832/2/144
3. Emmanuel E. Etim, Prsanta Gorai, Ankan Das and Arunan E, *Eur Phys J., D*, 2017, **71**, 86; DOI:10.1140/epjd/e2017-70611-3
4. Prasanta Gorai, Ankan Das, Amaresh Das, Bhalamurugan Sivaraman, Emmanuel E Etim and Sandip K Chakrabarti, *The Astrophys J.*, 2017, **836(1)**, 70; DOI:10.3847/1538-4357/836/1/70
5. Emmanuel E Etim and Arunan E, *Astrophys Space Sci.*, 2017, **362**, 4; DOI:10.1007/s10509-016-2979-6
6. Emmanuel E Etim and Arunan E, *Advn Space Res.*, 2017, **59(4)**, 1161-1171; DOI:10.1016/j.asr.2016.11.021
7. Emmanuel E Etim and Arunan E, *Eur Phys J Plus*, 2016, **131**, 448; DOI:10.1140/epjp/i2016-16448-0

8. Emmanuel E Etim, Prsanta Gorai, Ankan Das and Arunan E, *Adv Space Sci.*, 2017, **60(3)**, 709-721; DOI:10.1016/j.asr.2017.04.003
9. Didriche K and Herman M, *Chem Phys Lett.*, 2010, **496**, 1-7; DOI:10.1016/j.cplett.2010.07.031
10. Herman M, Liévin J, Vander Auwera J and Campargue A, *Adv Chem Phys.*, 1999, **108**, 1-43; DOI:10.1002/9780470141670.ch1
11. Herman M, Campargue A, El Idrissi M I and Auwera J V, *J Phys Chem Ref Data*, 2003, **32**, 921-1361; DOI:10.1063/1.1531651
12. Orr B J, *Int Rev Phys Chem.*, 2006, **25**, 655-718; DOI:10.1080/01442350600892577
13. Herzberg G, *Molecular Spectra and Molecular Structure*, Van Nostrand, New York, 1950.
14. Cane E, Cazzoli G, Di Lonardo G, Dore L, Escribano R and Fusina L, *J Mol Spectrosc.*, 2002, **216**, 447-453; DOI:10.1006/jmsp.2002.8623
15. Keppler K A, Mellau G C, Klee S, Winnewisser B P, Winnewisser M, Plíva J and Rao K N, *J Mol Spectrosc.*, 1996, **175**, 411-420; DOI:10.1006/jmsp.1996.0047
16. Kostyk E and Welsh H L, *J Phys.*, 1980, **58**, 534-543; DOI:10.1139/p80-074
17. Bermejo D, Cancio P, Fusina L and Di Lonardo G, *J Chem Phys.*, 1998, **108(17)**, 7224-7228; DOI:10.1063/1.476140
18. Huet T R, Herman M and Johns J W C, *J Chem Phys.*, 1991, **94(5)**, 3407-3414; DOI:10.1063/1.459763
19. Amyay B, Herman M, Fayt A, Fusina L and Predoi-Cross A, *Chem Phys Lett.*, 2010, **491**, 17-19; DOI:10.1016/j.cplett.2010.03.053
20. Girard V, Farrenq R, Sorokin E, Sorokina I T, Guelachvili G and Picqué N, *Chem Phys Lett.*, 2006, **419**, 584-588; DOI:10.1016/j.cplett.2005.12.029
21. Zhan X, Vaittinen O and Halonen L, *J Mol Spectrosc.*, 1993, **160**, 172-180; DOI:10.1006/jmsp.1993.1165
22. Robert S, Herman M, Fayt A, Campargue A, Kassi S, Liu A, Wang L, Di Lonardo G and Fusina L, *Mol Phys.*, 2008, **106(21-23)**, 2581-2605.
23. Campargue A, Abbouti-Temsamani M and Herman M, *Mol Phys.*, 1997, **90**, 793-805; DOI:10.1080/002689797172147
24. Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B and Petersson G A, Gaussian 09, Revision D.01. Gaussian, Inc., Wallingford, 2009.
25. Robert S, Herman M, Vander Auwera J, Di Lonardo G, Fusina L, Blanquet G, Lepe`re M and Fayt A, *Mol Phys.*, 2007, **105**, 559-568; DOI:10.1080/00268970601099261
26. Herzberg G, *Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules*, Chaps II-III, Reprint Ed., Krieger, Melbourne, FL, 1990.