SPIN MULTIPLICITY ON STRUCTURE AND VIBRATIONAL SPECTRUM OF CYANAMIDE

BHAGWAT KHARAT

Department of Physics, Swami Vivekanand Sr. College Mantha, Maharashtra, India. Email: Bhagwat6776@gmail.com

ABSTRACT

Objective: The geometrical optimization, vibrational spectrum of cyanamide in singlet, triplet and quintet state using Density functional Theory method.

Materials and Methods: The methods used here are MP2, MP3, MP4 and DFT method with different exchange and correlation functional (BLYP, B3LYP, B3PW91, PBEPBE, PBE1PBE) and different basis sets viz. 6-311G, 6-311+G, 6-311+G*, 6-311++G*, 6-311++G**, aug-cc-pvdz, aug-cc-pvtz and SDD to know at what level of theory cyanamide has the lowest energy. All the calculations are performed using Gaussian suit of program

Results: Cyanamide shows the lowest energy at B3LYP/aug-cc-pvdz level among different levels used here. The geometrical parameter and vibrational frequencies obtain at this level are in close agreement with the experimental determinations. Out of nine vibrational modes, seven modes in triplet and eight in quintet state are red shifted than those in a singlet state. The only blue shifted mode in quintet is the C-N stretching mode with a blue shifted of 220 cm^{-1} than that for the singlet.

Conclusion: The geometrical parameter and vibrational frequencies obtain at this level are in close agreement with the experimental determinations. The dipole moment decreases in higher spin state than the singlet

Keywords: Vibrational spectra, cyanamide, Density functional theory method.

INTRODUCTION

The cyanamide is an organic compound, which contains both, a nucleophilic and electrophilic site and is widely used for the production of organic compounds and pharmaceuticals as well as in agriculture. It bears great promise as a molecule for applications such as alcohol deterrent drug. The molecule features a nitriles group attached to an amino group. Kapellos et. al.[1] have obtained the structural parameters of cyanamide using ab initio methods. Tyler et. al.[2] fully characterised the microwave spectra of cyanamide. Vibrational spectra and the inversion phenomenon in cyanamide are calculated by Fletcher et. al.[3]. Wagner et. al.[5] studied the vibrational spectra and structure of monomeric cyanamide and deuterio-cyanamide. The pyramidal structure about the amino nitrogen of cyanamide has been confirmed experimentally by microwave and high resolutions Fourier Transform Infrared spectroscopy as well as theoretically [4,6-11]. Recently photo dissociation dynamics of cyanamide at 193 and 212 nm was reported [12-13]. The aim of this article is to study cyanamide in singlet, triplet and quintet state and to compare vibrational spectra in those three states. This paper is structured as follows. Next section gives computational details. Results are presented and discussed in the third section. It includes structure, vibrational spectra of cyanamide in singlet, triplet and quintet states. Conclusions are interred in the last section.

COMPUTATIONAL DETAILS

First we optimized the geometries of cyanamide in singlet state at different levels of theories. The methods used here are MP2, MP3, MP4 and DFT method with different exchange and correlation functional (BLYP, B3LYP, B3PW91, PBEPBE, PBE1PBE) and different basis sets viz. 6-311G, 6-311+G, 6-311+G*, 6-311++G*, 6-311++G**, aug-cc-pvdz, aug-cc-pvtz and SDD to know at what level of theory cyanamide has the lowest energy and agreement between theoretical and experimental structural parameters. We then optimized the geometries of cyanamide in triplet and quintet state at the same level of theory. Vibrational frequencies for singlet, triplet and quintet state

of cyanamide are also obtained at the same level of theory. All the calculations are performed using Gaussian suit of program [14].

RESULT AND DISCUSSION

We optimized the geometries of cyanamide in singlet state using different methods (HF, MP2, MP3 and DFT with BLYP, B3LYP, B3PW91, PBEPBE and PBE1PBE) and various basis sets. Table 1 represents the relative stability of cyanamide monomer. It was found that there is an excellent agreement between the geometrical parameters at B3LYP/aug-cc-pvdz level from this work and the experimental determinations [2, 9]. As can be seen from Table 1, cyanamide monomer has the lowest energy at B3LYP/aug-cc-pvdz level of theory. Next, we optimized the geometries of cyanamide in triplet and quintet state at the same level of theory viz. B3LYP/aug-cc-pvdz to compare our results with those for cyanamide in singlet state.

Table 1: Relative stability ΔE (Kcal/mol) of cyanamide with aug-cc-pvdz basis set.

Method	ΔE
HF	-547.89
MP2	-254.09
MP3	-251.2
BLYP	-23.86
B3LYP	0
B3PW91	-38.55
PBEPBE	-109.1
PBE1PBE	-109.21

The structural parameters of cyanamide in singlet, triplet and quintet state at B3LYP/aug-cc-pvdz level alongwith available experimental determinations [17, 24] are represented in Table 2. There is an excellent agreement between the structural parameters from this work at B3LYP/aug-cc-pvdz level and experimental determinations for the singlet state. The calculated dipole moment at this level is also in agreement with the available experimental value. The C-N bond is

shortened to 1.345 Å in triplet and little elongated to 1.348 Å in quintet as compared to that for the singlet state. The calculated N-H bond length is elongated in triplet and quintet state than that for the singlet state. Significant change in the $C\equiv N$ bond length is observed in higher spin state. As can be seen from Table 2, the $C\equiv N$ bond length is longer by 0.127 Å and 0.403 Å in triplet and quintet state respectively than the singlet state. $\angle HNH$ is increased by 4.7° and 2.3° in triplet and quintet state respectively than that for the singlet, and also in

excellent agreement with the experimental value for the singlet. The $\angle CNH$ is increased by 5.6° and 7.3° in triplet and quintet respectively than the singlet state. The $\angle NCN$ is decreased by 55.9° in triplet and 60.7° in quintet than the singlet state. The dipole moment in singlet is 4.6 Debye which is agreement with the two reported experimental values of 4.32 and 4.25 Debye. The dipole moment decreases in higher spin state than the singlet.

Table 2: Geometrical parameters for singlet, triplet, and quintet of cyanamide atB3LYP/aug-cc-pvdz level of theory along with experimental values.

Parametera	Expt. Value		Singlet	Triplet	Quinte
	a	b			
N-H	1.001	1.008	1.014	1.022	1.019
C-N	1.345	1.35	1.347	1.345	1.348
$C\equiv N$	1.16	1.165	1.165	1.292	1.568
$H-N-H\angle$	113.3	112.8	113.1	117.8	115.4
$H-N-X\angle$	115.6	113	115	120.6	122.3
$N-X-N\angle$	180	174.8	177	121.1	116.3
Dipole moment	4.32	4.25	4.6	4.39	3.12

Bond length are in Å and angles in °, [a] Ref. [2]   [b] Ref. [9]]

Vibrational frequencies, corresponding mode assignments and IR intensities for the cyanamide in singlet, triplet and quintet state at B3LYP/aug-cc-pvdz level are collected in Table 3 alongwith experimental vibrational frequencies for the cyanamide in singlet state [18, 19]. All the vibrational frequencies represented here are the unscaled frequencies. As can be seen from Table 3, there is a close agreement between the calculated and experimental vibrational frequencies. The $C\equiv N$ stretching mode in most of the nitriles is observed within a range of 2325-2125cm^{-1} [32]. Cyanamide in singlet state displays a $C\equiv N$ stretching feature at 2345 cm^{-1}. It is the second intense mode in vibrational spectrum of the singlet state of

cyanamide. The most intense mode in the vibrational spectrum of cyanamide in singlet state is the NH$_2$ wagging mode appearing at 553 cm^{-1}. Apart from these two modes, features at 480, 1611, 3535 and 3634 cm^{-1} are also quite intense which correspond to the NCN in plane bending, NH$_2$ scissoring, NH$_2$ symmetric stretching and NH$_2$ asymmetric stretching mode respectively. As compared to the $C\equiv N$ stretching mode, the C-N stretching mode appearing at 1090 cm^{-1} is much weaker. The two modes of negligible IR intensity in vibrational spectrum of a singlet are the NCN out plane bending and NH$_2$ rocking mode appearing at 401 and 1182 cm^{-1} respectively.

Table 3: Vibrational frequencies in (cm^{-1}) and IR intensities are in (km mol^{-1}) for singlet, triplet and quintet of cyanamide at B3LYP/aug-cc-pvdz level of theory alongwith experimental values for the ground state.

Vibrational Frequencies (cm-1)				
Expt.	Singlet	Triplet	Quintet	Assignment
437 a	401(0)	328(17)	-----	NCN out plane bend
538 a	480(75)	475(14)	409(15)	NCN in plane bend
----	553(143)	603(138)	280(155)	NH2 Wagg
1130 a	1090(9)	1201(18)	1310(12)	C-N stretch
926 a	1182(0)	1071(0.5)	1033(6)	NH2 rock
1586 a	1611(37)	1603(40)	1600(30)	NH2 scissor
2275b	2345(115)	1475(12)	783(5)	$C\equiv N$ stretch
3420b	3535(38)	3408(6)	3420(8)	NH2 sym stretch
3469b	3634(62)	3614(61)	3508(14)	NH2 asym stretch

[a] Ref. [3]   [b] Ref.[4]

Almost all the vibrational modes in a triplet as well as quintet state are red shifted than the corresponding modes in singlet state except the NH$_2$ wagging and C-N stretching modes in triplet and the C-N stretching mode in quintet. In triplet as well as quintet state the red shifts are larger than the blue shifts. The highest and lowest red shift of 870 and 05 cm^{-1} is obtained for the $C\equiv N$ stretching and NCN in plane bending mode respectively, for the triplet than the singlet state. The NH$_2$ wagging and C-N stretching modes are blue shifted by 50 and 111 cm^{-1} respectively in triplet than the singlet. The only blue shifted mode in quintet state is the C-N stretching mode. It is blue shifted by 220 cm^{-1} in quintet state than the singlet state. The highest and lowest red shift of 1562 and 11 cm^{-1} is obtained for the $C\equiv N$ stretching and NH$_2$ scissor modes respectively for quintet state than the singlet.

For triplet, the most intense mode is the NH$_2$ wagging mode which appeared at 603 cm^{-1}. However, this mode is slightly less intense in triplet state and is blue shifted by 50 cm^{-1} than the singlet state. The second intense mode is different in singlet and triplet state. It is the $C\equiv N$ stretching in the former and NH$_2$ asymmetric stretching mode in the latter. A red shift of 20 cm^{-1} for the NH$_2$ asymmetric stretching mode is observed in triplet state than the singlet. The NH$_2$ scissor is

the third intense mode in triplet and appeared at 1603 cm^{-1}. This mode is red shifted by 8 cm^{-1} in triplet than singlet state. The NH$_2$ rocking mode of negligible IR intensity in singlet is of negligible IR intensity in triplet state also and red shifted by 111 cm^{-1}in triplet than the singlet. Other modes of significant IR intensity in triplet state are the NCN out plane bending, NCN in plane bending, C-N stretching and NH$_2$ symmetric stretching mode appearing at 328, 475, 1201 and 3408 cm^{-1} respectively. Out of these four modes, NCN out of plane bending, NCN in plane bending, NH$_2$ symmetric stretching mode are red shifted by 73, 05 and 127 cm^{-1} respectively in triplet state than the singlet. The C-N stretching mode is blue shifted by 111 cm^{-1} in triplet state than the singlet.

The most intense mode in singlet, triplet and quintet state is the same which is the NH$_2$ wagging mode. In quintet state, this mode is appeared at 280 cm^{-1} and red shifted by 273 cm^{-1} than the singlet state. The second intense mode in quintet state is the NH$_2$ scissoring mode appearing at 1600 cm^{-1}. It is red shifted by 11 cm^{-1} in quintet that the singlet. It was the sixth intense mode in singlet and third intense in the triplet state. However, it is weak in quintet than the singlet and triplet state. The third intense mode is the same in singlet and quintet state which is the NCN in plane bending mode appearing

at 409 cm^{-1} in quintet state. It is red shifted by 71 cm^{-1} and is about five times less intense in quintet than the singlet state. The NH$_2$ asymmetric stretching mode appearing at 3508 cm^{-1} is the fourth intense mode in quintet state as well as singlet state. However it is about four times weak in quintet than the singlet and red shifted by 126 cm^{-1} in quintet state. Other modes of significant IR intensity in quintet state are the C-N stretching, NH$_2$ symmetric stretching, NH$_2$ rocking and C≡N stretching modes appearing at 1310, 3420, 1033 and 783 cm^{-1} respectively. Out of these four modes, the NH$_2$ symmetric stretching, NH$_2$ rocking and C≡N stretching mode are red shifted by 115, 149 and 1562 cm^{-1} respectively in quintet state than the singlet. The C-N stretching mode is blue shifted by 220 cm^{-1} in quintet state than singlet. The first intense mode in singlet, triplet and quintet state, the NH$_2$ wagging mode is of comparable IR intensity however it appeared at different position in their vibrational spectrum.
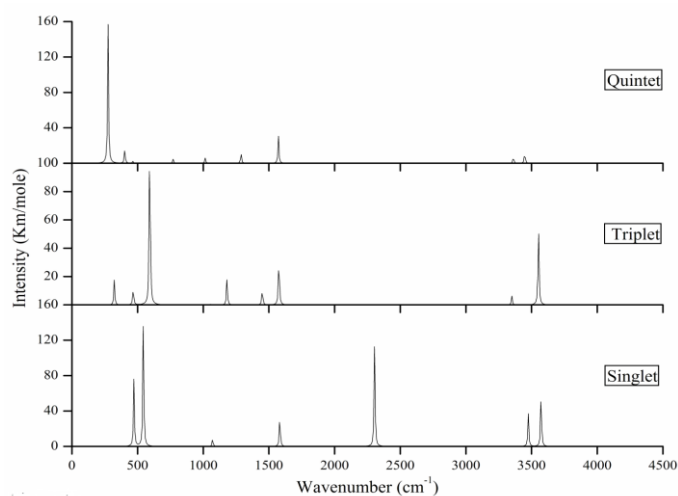

Fig.1: Vibrational spectra of cyanamide in singlet, triplet and quintet state obtained at B3LYP/aug-cc-pvdz level.

CONCLUSION

We have studied the effects of spin multiplicity on structure, vibrational spectrum for cyanamide using quantum chemical methods. The optimized geometries at B3LYP/aug-cc-pvdz are in excellent agreement with the experimental determinations. The geometrical parameter and vibrational frequencies obtain at this level are in close agreement with the experimental determinations. Out of nine vibrational modes, seven modes in triplet and eight in quintet state are red shifted than those in a singlet state. The only

blue shifted mode in quintet is the C-N stretching mode with a blue shifted of 220 cm^{-1} than that for the singlet. The dipole moment in singlet is 4.6 Debye which is in agreement with the two reported experimental values of 4.32 and 4.25 Debye. The dipole moment decreases in higher spin state than the singlet.

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