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Infrared and electronic absorption spectra of n-butyronitrile and its ions using Møller Plesset method

Mahadevappa Naganathappa · Ajay Chaudhari

Abstract We report theoretical infrared and electronic absorption spectra of gauche and anti conformers of n-butyronitrile, their ions and 2-methylpropanenitrile isomer of n-butyronitrile. The coupled cluster theory (CCSD) and second order Møller-Plesset perturbation (MP2) theory with TZVP basis set are used for the study. Vibrational frequencies of gauche and anti conformers of neutral n-butyronitrile at MP2/TZVP and CCSD/TZVP levels are in agreement with the experimental determinations. Rotational and distortion constants are also in good agreement with the available experimental values. Time dependent density functional theory is used to study the electronic absorption spectra of gauche and anti conformers, their ions and an isomer of butyronitrile. All the electronic transitions of gauche and anti conformers of neutral n-butyronitrile and 2-methylpropanenitrile are $\sigma \rightarrow \sigma^*$ transitions whereas ions of n-butyronitrile show both $\sigma \rightarrow \sigma^*$ as well as $\pi \rightarrow \pi^*$ transitions in vacuum UV, far UV and visible regions. This study helps in detection of neutral gauche and anti conformer and their ions in interstellar medium.

Keywords n-butyronitrile · 2-methylpropanenitrile · Electronic absorption spectra · Electronic transitions · Quantum chemical method · Vibrational spectra

Introduction

The interstellar medium (the space between the stars) and intergalactic medium (the space between galaxies) do contain a certain level of matter in the form of gas and tiny solid particles. Since atoms are present in these media, chemistry can take place and molecules can be formed. To date more than 170 molecules are detected in interstellar medium. More than 50 % of the molecules are detected in Sagittarius B2 (Sgr B2) a giant molecular cloud which is one of the harbor for the complex organic molecules. It is very massive with several million solar mass and an extremely active region of high mass star formation. The organic molecules survive in this region because of the fruitful conditions such as density and temperature. Recently new organic molecules with more than eight atoms such as glycolaldehyde, vinyl alcohol, ethylene glycol, aminoacetonitrile, ethyl formate and butyronitrile are detected in space [1–6]. Ions and deuterated molecules are also detected in space [7–9]. Interstellar medium is composed of not only neutral molecules but also ions, deuterated and doubly deuterated forms of complex organic molecules. Many more molecules can be detected in space if we have their complete spectroscopic characterization. Quantum chemical methods can help to predict the infrared and electronic absorption spectra of complex organic molecules.

N-butyronitrile, one of the complex organic molecules, has recently been detected in Sgr B2 [6]. The common names for the n-butyronitrile are n-propyl cyanide, n-buranenitrile with molecular formula C_3H_7CN. The rotational spectrum of butyronitrile has been studied by Hirota *et al.* in microwave region up to 300 GHz [10]. The computer controlled spectrometer with superheterodyne instrument was used to report the centrifugal distortion constant and dipole moment of n-butyronitrile [11]. According to Durig *et al.* butyronitrile has two conformers, anti and gauche, and the latter is lower in energy than the former [12]. Two conformers of n-butyronitrile and its 2-methylpropanenitrile isomer are shown in Fig. 1.

M. Naganathappa · A. Chaudhari (✉)
School of Physical Sciences,
Swami Ramanand Teerth Marathwada University,
Nanded,
431606 Maharashtra, India
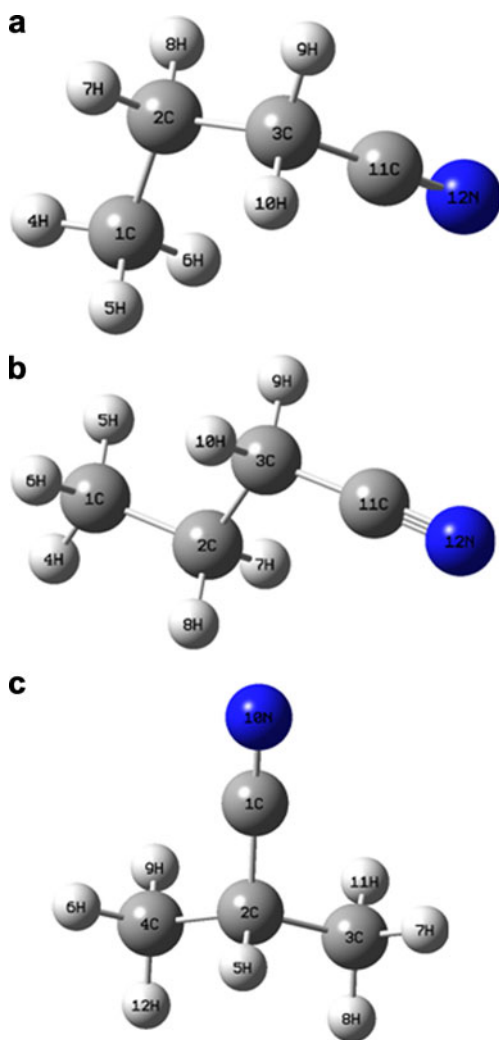e-mail: ajaychau5@yahoo.com

Fig. 1 a Gauche conformer b anti conformer c 2-methylpropanenitrile isomer of n-butyronitrile optimized at CCSD/TZVP level of theory

Durig *et al.* have reported vibrational spectrum of neutral conformer (3500-50 cm^{-1}), conformational stability and thermodynamical parameters [12]. Thomas *et al.* have reported Gibbs free energy, ionization energy for methyl group, photoelectron spectra and intensity ratio of anti and gauche conformers of butyronitrile [13].

The present study reports theoretical infrared and electronic absorption spectra of neutral, cation and anion of anti and gauche conformers of butyronitrile. We have also studied here spectroscopic fingerprints of the neutral 2-methylpropanenitrile isomer of butyronitrile. Since molecule may be in neutral or ionic form depending upon the physical conditions, it is necessary to have knowledge of their spectra in neutral as well as ionic form in order to detect molecules in space. In this study we compare theoretical and experimental vibrational spectra of neutral anti and gauche conformer of butyronitrile. For comparison, vibrational and absorption spectra of 2-methylpropanenitrile isomer of n-butyronitrile are also given. This paper is organized as follows. The next

section gives computational details. Infrared and electronic absorption spectra of n-butyronitrile and its isomer are discussed in Result and Discussion section. Conclusions are inferred in the last section.

Computational details

Geometries of gauche and anti conformers of n-butyronitrile and its isomer 2-methylpropanenitrile are optimized at coupled cluster theory (CCSD) [14–17] and second order Møller-Plesset (MP2) perturbation theory [18–22] using TZVP basis set. The gauche and anti conformers of neutral butyronitrile are obtained on the basis of $C_1C_2C_3C_{11}$ dihedral angle [12]. Vibrational frequencies for neutral conformers of butyronitrile and its isomer are obtained at both CCSD/TZVP and MP2/TZVP level of theory. All the frequencies reported here are scaled by a factor of 0.964. Time dependent density functional theory (TDDFT) calculations were performed for excited states of neutral and charged butyronitrile at the same levels. The nature of electronic transitions was identified. SWizard program was used to obtain % contribution from each transition [23]. All the calculations were performed using Gaussian 03 program package [24].

Results and discussion

Figure 1 shows the optimized structure of gauche and anti conformers and 2-methylpropanenitrile isomer of n-butyronitrile at CCSD/TZVP level. At CCSD (MP2) level of theory, the anti conformer is lower in energy by 0.27 kcal mol^{-1} (0.48 kcal mol^{-1}) than the gauche conformer which is in agreement with the experimental determination of the 0.2629±0.0717 kcal mol^{-1} [11]. The enthalpy difference between gauche and anti conformer is 0.45 kcal mol^{-1} (0.47 kcal mol^{-1}) at CCSD (MP2) level. This is also in agreement with the experimental determination of 0.2430±0.1944 kcal mol^{-1} reported from electron diffraction study by Traetteberg *et al.* [25]. The geometries of neutral gauche and anti conformers of n-butyronitrile are optimized using both, MP2 and CCSD methods. The ionization energy and electron affinity of gauche and anti conformer of n-butyronitrile are 271.7 kcal mol^{-1}, 51.14 kcal mol^{-1} and 271.2 kcal mol^{-1}, 52 kcal mol^{-1} respectively. Since our MP2 results for neutral anti and gauche conformers are close to those obtained at CCSD level, the ions of these conformers are optimized at MP2/TZVP level only.

There is no large difference in optimized geometries of gauche and anti conformers except the dihedral angle $C_1C_2C_3C_{11}$ which is 59.8° in the former and 179.9° in the latter. The dipole moment of gauche and anti conformers of neutral n-butyronitrile are 4.03(4.3) and 3.91(4.4) D respec-

tively at CCSD(MP2) level and comparable with the respective experimental values of 3.909 D and 3.729 D [11]. The dipole moment for the 2-methylpropanenitrile isomer of butyronitrile is 3.95 D which is close with the gauche conformer of butyronitrile.

The C≡N bond length is equal (1.170 Å) in neutral anti and gauche conformers whereas this bond is a little shorter in 2-methylpropanenitrile isomer of n-butyronitrile. The C-C bond lengths are longer in 2-methylpropanenitrile than those in anti and gauche conformers. Almost all bond lengths and angles in anti and gauche conformers are equal except the C-C-C-C dihedral angle. It is 67° and 179° in anti and gauche conformer, respectively. The C-C-C-C dihedral angle for 2-methylpropanenitrile is -62°.

Larger change is observed in some bond lengths and angles upon ionization of neutral gauche and anti conformers of n-butyronitrile. The change is larger for cation than the anion in both the conformers. In the following discussion *C represents carbon atom adjacent to the C≡N bond. The bond lengths in neutral gauche conformer and its

ions differ in the range of 0.006-0.058 Å with the exception of $^*C_3C_2$ bond. The $^*C_3C_2$ bond length is longer by 0.37 Å and 0.19 Å in cation than that of neutral gauche and anti conformer respectively. Significant change in bond angles upon ionization is observed. The $^*C_3C_2H_7$ angle is smaller by 13.4° in cation than the corresponding angle in neutral gauche conformer. In case of anion $^*C_3C_{11}N$ angle is smaller by 15.9° than the corresponding angle in neutral gauche conformer. For anti conformer the bond distances in neutral and ions differ in the range of 0.003 to 0.189 Å. The $^*C_3C_2C_{11}$ and $^*C_3C_{11}N$ angles are smaller by 12.7° and 14.6° in cation and anion respectively than the corresponding angles in neutral anti conformer of butyronitrile. The highest change in dihedral angle $C_1C_2{}^*C_3C_{11}$ by 180° is observed in cation of anti conformer.

Infrared spectra

The vibrational modes of neutral gauche and anti conformers of n-butyronitrile at MP2/TZVP and CCSD/TZVP

Table 1 Vibrational modes for neutral gauche and anti conformers of n-butyronitrile at MP2 and CCSD levels along with the experimental values. Values in parenthesis are absorption coefficients

Mode	Gauche (Neutral)			Anti (Neutral)		
	[a]Expt	MP2	CCSD	[a]Expt	MP2	CCSD
*C-C-C bend	358	339(1.2)	361(0.1)	351	332(0.05)	333(0.09)
N≡C-C bend	559	538(0.3)	541(0.3)	528	503(0.6)	507(0.6)
CH₂ rock	778	749(1)	748(0.4)	741	730(1.7)	729(1.3)
*C-C-C symm. stretch	842	835(1.1)	832(1.4)	1110	863(1.6)	861(0.1)
*CH₂ rock	871	867(1)	868(1)	871	860(0.1)	—
≡C-C stretch	920	907(2.2)	906(2.5)	945	936(1.4)	932(2)
*C-C-C asymm stretch	1053	1044(0.5)	1044(0.3)	1048	1040(1.5)	1036(0.09)
CH₃ rock	1083	1077(0.5)	1082(0.3)	1091	1096(1.5)	1110(0.009)
*CH₂ twist	1234	1224(0.9)	1232(0.9)	1233	1233(0.02)	1238(0.02)
CH₂ twist	1267	1259(0.4)	1267(0.3)	1279	1296(0.1)	1285(2.5)
*CH₂ wag	1334	1330(1.8)	1343(2.2)	—	1273(1.5)	1299(0.1)
CH₂ wag	1346	1345(2.7)	1357(3)	1347	1365(2)	1379(1.6)
CH₃ symm. deform	1393	1393(4.8)	1399(3.8)	1387	1388(2.5)	1400(1.6)
*CH₂ scissor	1438	1436(6.5)	1447(5.6)	1440	1441(3.3)	1448(2.7)
CH₂ scissor	1457	1455(1.3)	1462(0.9)	1457	1459(1.3)	1463(0.9)
CH₃ asymm. deform	1469	1464(7)	1470(6.3)	1469	1467(8)	1470(6)
CH₃ asymm. deform	1472	1473(7.4)	1477(5.7)	1472	1474(7)	1478(6)
C≡N stretch	2263	2133(0.15)	2274(1.1)	2261	2135(0.02)	2275(1.6)
CH₃ symm. Stretch	2888	2972(14.7)	2953(18.7)	2883	2972(18)	2951(21)
CH₂ symm. Stretch	2888	2986(23)	2966(23)	2883	2996(23)	2971(3)
*CH₂ symm. Stretch	2888	2988(6.7)	2968(6.8)	2895	2986(0.07)	2979(23)
*CH₂asymm. stretch	2950	3044(4.4)	3022(10)	2950	3045(0.02)	3001(0.1)
CH₃ asymm. stretch	2986	3067(32)	3029(39)	2956	3065(42)	3017(5.6)
CH₂ asymm.stretch	2964	3059(22)	3036(32)	2979	3062(22)	3031(30)

*C represents CH2 group adjacent to the C≡N stretch, **a** represents expt. data taken from ref. [12]

level of theory with the available experimental values are summarized in Table 1. The vibrational frequencies at both the levels are in good agreement with the available experimental frequencies [12]. The modes at MP2 and CCSD levels differ in the range of 10 to 15 cm⁻¹ in gauche as well as anti conformer with the exception of the C≡N stretch, CH₃ asymmetric stretch, *CH₂ asymmetric stretch and CH₂ asymmetric stretch. In neutral gauche conformer these modes differ by 141, 38, 22 and 23 cm⁻¹ and in neutral anti conformer these four modes differ by 140, 48, 44 and 31 cm⁻¹. The intensity of most of the modes is almost the same for both the conformers at both the levels. Since the vibrational frequencies obtained at MP2 level are comparable with the CCSD level, we have discussed vibrational frequencies at MP2 level only.

The vibrational modes of gauche and anti conformers of n-butyronitrile and their ions are given in Table 2 and their respective infrared spectra are shown in Fig. 2a and b. The most intense peak observed in neutral gauche and anti conformer is at 3067 cm⁻¹ (3.260 μm) and 3062 cm⁻¹ (3.265 μm) respectively which corresponds to the CH₃ asymmetric stretch and CH₂ asymmetric stretch mode. In neutral anti and gauche conformers, the CH₂ symmetric stretch is the second intense mode. It appears at 2986 cm⁻¹ (3.348 μm) and 2996 cm⁻¹ (3.337 μm) in gauche and anti conformers respectively. However the third intense mode is different for neutral gauche and anti conformers. In former it is the CH₂ asymmetric stretch which appears at 3059 cm⁻¹ (3.269 μm) and in latter it is the CH₃ asymmetric stretch appearing at 3065 cm⁻¹ (3.262 μm). The vibrational modes of gauche and anti conformers of n-butyronitrile differ in the range of 5-10 cm⁻¹ with the exception of the *CH₂ wag, N≡C-C bend, CH₂ twist, and ≡C-C stretch modes which appear at 1330 cm⁻¹ (7.692 μm), 538 cm⁻¹ (18.587 μm), 1259 cm⁻¹ (7.942 μm) and 907 cm⁻¹ (11.025 μm) respectively in gauche conformer. The *CH₂ wag mode is red shifted by 57 cm⁻¹ in anti conformer than that in gauche conformer whereas the N≡C-C bend mode is red shifted by 35 cm⁻¹ in anti

Table 2 Vibrational modes for neutral gauche and anti conformers of n-butyronitrile and their ions at MP2/TZVP level of theory. Values in parenthesis are absorption coefficients

Mode	Gauche			Anti		
	Neutral	Cation	Anion	Neutral	Cation	Anion
*C-C-C bend	339(1.2)	354(104)	390(100)	332(0.05)	402(0.1)	370(36)
N≡C-C bend	538(0.3)	493(3.7)	606(237)	503(0.6)	432(80)	616(486)
CH₂ rock	749(1)	739(219)	718(80)	730(1.7)	705(1.1)	651(493)
*C-C-C symm stretch	835(1.1)	—	866(166)	863(1.6)	664(0.9)	880(555)
*CH₂ rock	867(1)	821(23)	834(100)	860(0.1)	824(0.5)	850(0.1)
≡C-C stretch	907(2.2)	987(219)	917(349)	936(1.4)	1035(3.8)	907(477)
*C-C-C asymm.stretch	1044(0.5)	1049(54)	1043(157)	1040(1.5)	952(122)	1046(119)
CH₃ rock	1077(0.5)	—	1108(266)	1096(1.5)	840(335)	1100(166)
*CH₂ twist	1224(0.9)	1060(.02)	1201(247)	1233(.02)	824(0.55)	1077(21)
CH₂ twist	1259(0.4)	1208(3.6)	1245(326)	1296(0.1)	1204(0.4)	1292(0)
*CH₂ wag	1330(1.8)	1098(6.2)	1343(345)	1273(1.5)	1156(25)	1245(867)
CH₂ wag	1345(2.7)	1179(185)	1356(332)	1365(2)	1258(81)	1290(520)
CH₃ symm deform	1393(4.8)	1305(39)	1325(13)	1388(2.5)	1347(9.3)	1318(96)
*CH₂ scissor	1436(6.5)	1415(2)	1276(438)	1441(3.3)	1409(19)	—
CH₂ scissor	1455(1.3)	1446(7.4)	1414(95)	1459(1.3)	1452(6.3)	1433(15)
CH₃ asymm deform	1464(7)	1356(23)	1435(51)	1467(8)	1376(18)	1438(0.8)
CH₃ asymm deform	1473(7.4)	—	1467(29)	1474(7)	—	1474(196)
C≡N stretch	2133(0.15)	2498(1560)	2677(5595)	2135(.02)	2330(4022)	2891(19224)
CH₃ symm. stretch	2972(14.7)	2829(165)	2891(547)	2972(18)	2900(139)	2881(4312)
CH₂ symm. stretch	2986(23)	3026(20)	2953(192)	2996(23)	3029(29)	2709(3477)
*CH₂ symm. stretch	2988(6.7)	3043(17)	2706(1359)	2986(.07)	3041(4.7)	2914(6318)
*CH₂asymm. stretch	3044(4.4)	3149(33)	2634(3340)	3045(.02)	3122(19)	2739(1569)
CH₃ asymm. stretch	3067(32)	3037(15)	2985(47)	3065(22)	3055(16.8)	2985(3717)
CH₂ asymm.stretch	3059(22)	3130(0.8)	3025(425)	3062(42)	3134(15)	2960(284)

*C represents CH2 group adjacent to the C≡N stretch, a represents expt. data taken from ref. [12]

cation, and anion. **b** infrared spectrum of anti conformer of n-butyronitrile, its cation, and anion. **c** comparative IR spectra of anti, gauche conformer and 2-methylpropanenitrile isomer of n-butyronitrile

conformer. Also the CH_2 twist, and $\equiv$C-C stretch modes are blue shifted by 37 and 29 cm^{-1} respectively in anti conformer than the gauche conformer.

Large change is observed in infrared spectra and absorbance upon ionization of gauche conformer of n-butyronitrile. C_1 is the highest symmetry for the neutral gauche conformer of n-butyronitrile. Apart from the first three intense modes viz. the CH_3 asymmetric stretch, CH_2 symmetric stretch and CH_2 asymmetric stretch in neutral gauche conformer, the CH_3 symmetric stretch, CH_3 asymmetric deformation and $^*CH_2$ symmetric stretch are also intense and comparable with the experimental values [12]. The most intense peak observed in cation of gauche conformer is the C$\equiv$N stretching mode which appears at 2498 cm^{-1} (4.003 μm). This mode was much less IR active in neutral gauche conformer and is blue shifted by 365 cm^{-1} in cation than the neutral. The most intense mode in neutral gauche conformer, the CH_3 asymmetric stretching mode, is less IR active in cation than the neutral conformer and is red shifted by 30 cm^{-1}. Other modes whose IR intensity significantly increases in cation than that of neutral are the CH_2 rock [739 cm^{-1} (13.531 μm)], $^*CH_2$ rock [821 cm^{-1} (12.180 μm)], $\equiv$C-C stretch [987 cm^{-1} (10.131 μm)], *C-C-C asymmetric stretch [1049 cm^{-1} (9.532 μm)], CH_2 wag [1179 cm^{-1} (8.481 μm)], CH_3 symmetric deformation [1305 cm^{-1} (7.662 μm)], CH_3 asymmetric deformation [1356 cm^{-1} (7.374 μm)], CH_3 symmetric stretch [2829 cm^{-1} (3.534 μm)], and $^*CH_2$ asymmetric stretch [3149 cm^{-1} (3.175 μm)]. Large blue/red shift is also observed in these modes upon ionization. The *C-C-C bend, $\equiv$C-C stretch and $^*CH_2$ asymmetric stretching modes are blue shifted by 15, 80 and 105 cm^{-1} respectively. On the other hand the CH_2 rock, $^*CH_2$ rock, CH_2 wag, CH_3 symmetric deformation, CH_3 asymmetric deformation and CH_3 symmetric stretching modes are red shifted by 10, 46, 166, 88, 108 and 143 cm^{-1} respectively.

Similar to cation, in anion of gauche conformer also the C$\equiv$N stretching mode is dominant in infrared spectrum with highest intensity among all the vibrational modes. The blue shift in the C$\equiv$N stretching mode in anion is large viz. 544 cm^{-1} than that in cation. The IR intensity for this mode in anion is more than thrice than the cation. Almost all the vibrational modes for anion of gauche conformer are intense. The modes which were less intense in cation are also intense in anion. The $^*CH_2$ asymmetric stretching mode which was less intense in cation now becomes second intense mode in anion.
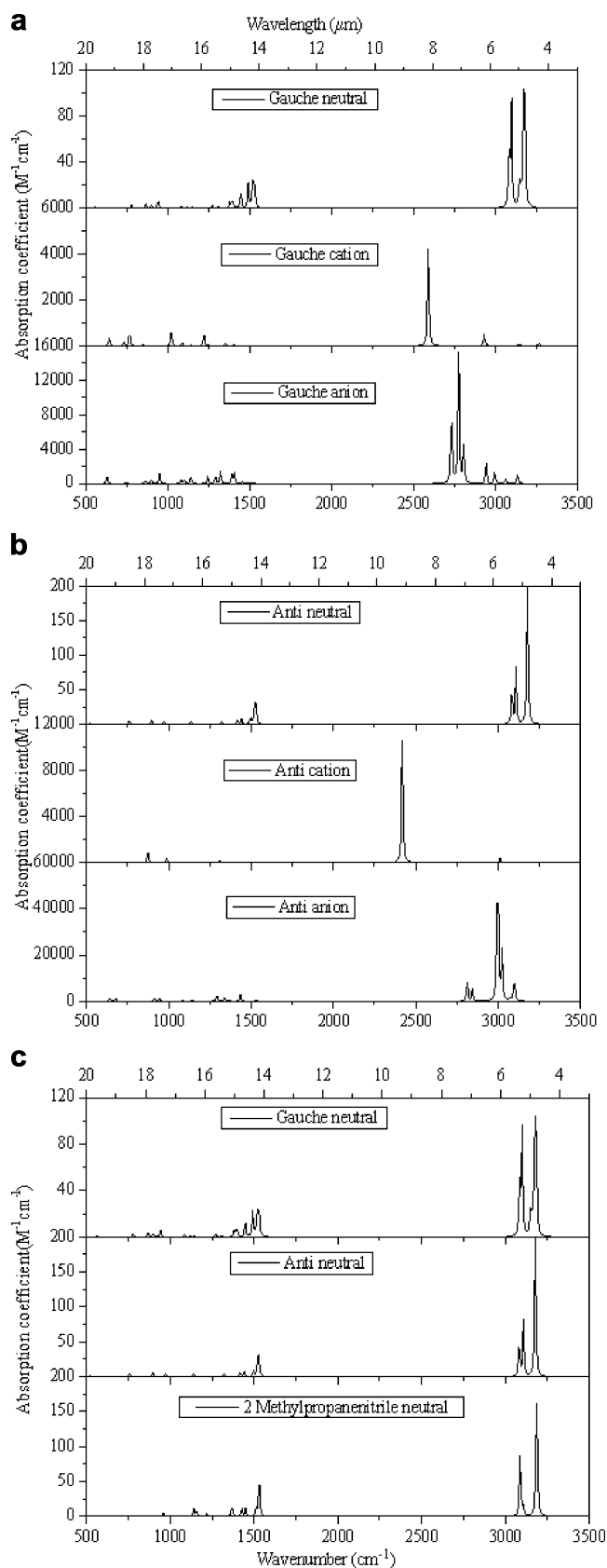
Table 3 Vibrational frequencies (cm^{-1}), rotational and centrifugal distortion constants of neutral 2-methylpropanenitrile isomer of n- butyronitrile at MP2/TZVP and CCSD/TZVP levels

Mode	Vibrational frequencies		Rotational and distortion constants		
	MP2	CCSD	Constant	MP2	CCSD
N≡C-C bend	525(0.6)	530(0.6)	A (MHz)	8003.6	7969.1
N≡C-C bend	542(0.3)	549(0.1)	B (MHz)	3968.4	3962.3
N≡C-Cstretch	759(0.4)	753(1)	C (MHz)	2913.4	2903.3
CH$_2$ rock	923(1.1)	959(0.8)	Δ_J (KHz)	0.9688	0.9368
CH$_2$ rock	959(0.1)	960(0.1)	Δ_{JK}(KHz)	10.265	9.4460
CH$_3$ rock	1099(3.5)	1106(3.5)	Δ_K (KHz)	-3.706	-3.0004
C-C-C asymm.stretch	1116(2.8)	1119(2.6)	δ_J (KHz)	0.2327	0.2284
C-C-C asymm.stretch	1174(1.4)	1179(1.5)	δ_K (KHz)	6.5173	6.0526
CH in plane stretch to CCC mode	1300(0.2)	1314(0.3)	Φ_J (mHz)	0.9117	
CH in plane stretch to CCC mode	1318(5.4)	1331(6.8)	Φ_k (Hz)	0.5218	
CH$_3$ symm.deform	1374(3.6)	1388(2.4)	Φ_{JK} (mHz)	82.89	
CH$_3$ symm.deform	1397(3.6)	1409(2.8)	Φ_{KJ} (Hz)	-0.598	
CH$_2$ Scissor	1453(0.5)	1458(0.3)	Φ_j (mHz)	0.2269	
CH$_2$ Scissor	1458(3.2)	1462(2.7)	Φ_k (Hz)	-0.044	
CH$_3$ asymm. deform	1471(5.4)	1475(4.8)	Φ_{JK} (mHz)	44.49	
CH$_3$ asymm. deform	1475(12.8)	1480(10)			
C≡N stretch	2126(0.08)	2270(1.2)			
CH$_3$ symm. stretch	2977(15)	2959(16)			
CH$_3$ symm. stretch	2978(13)	2961(15)			
CH stretch	2994(4.5)	2978(4)			
CH$_2$ asymm. stretch	3069(33)	3039(44)			
CH$_3$ asymm. stretch	3073(12)	3042(16)			
CH$_3$ asymm. stretch	3074(18)	3044(24)			

However, the CH$_2$ rock and CH$_3$ symmetric deformation modes become less intense in anion than the cation. The CH$_2$ asymmetric stretching mode in anion appears at 3025 cm^{-1} which is blue shifted by 34 cm^{-1} than the neutral and the IR intensity for this mode is about twenty times higher than that of neutral. A large red shift of 410 cm^{-1} is observed for the *CH$_2$ asymmetric stretching mode than the corresponding mode in neutral.

Table 4 Rotational and centrifugal distortion constants for the two conformers of neutral n-butyronitrile at MP2/TZVP and CCSD/TZVP levels alongwith the available experimental results

Mode	Gauche (neutral)			Anti (neutral)		
	Expt[a]	MP2	CCSD	Expt[a]	MP2	CCSD
A (MHz)	10060.38	9915.56	10034.45	23667.84	23742.84	23826
B (MHz)	3267.66	3338.15	3275.72	2268.14	2273.59	2264.2
C (MHz)	2705.44	2739.32	2707.88	2152.96	2157.90	2150.3
Δ_J (KHz)	3.35	3.59	3.33	0.400	0.408	0.384
Δ_{JK}(KHz)	-19.20	-21.16	-20.44	-10.84	-12.19	-10.91
Δ_K (KHz)	61.12	59.41	61.03	219.5	261.33	241.4
δ_J (KHz)	1.03	1.13	1.04	0.046	0.049	0.045
δ_K (KHz)	7.90	6.88	6.84	0.269	0.709	0.547
Φ_J (mHz)	6.99	5.52	—	0.457	0.410	—
Φ_k (Hz)	0	0.78	—	0	-10.75	—
Φ_{JK} (mHz)	28.00	-70.67	—	0	-60.03	—
Φ_{KJ} (Hz)	-0.49	-0.081	—	0.291	0.914	—
Φ_j (mHz)	2.44	2.62	—	0	0.113	—
Φ_k (Hz)	0	0.44	—	5.59	2.78	—
Φ_{JK} (mHz)	0	-0.085	—	0	-6.30	—

[a] represents expt. data taken from ref. [11]

Fig. 3 a Electronic absorption spectra of gauche conformer of n-butyronitrile, its cation, and anion. **b** electronic absorption spectra of anti conformer of n-butyronitrile, its cation, and anion. **c** electronic absorption spectrum of neutral 2 methyl-propanenitrile isomer of n-butyronitrile
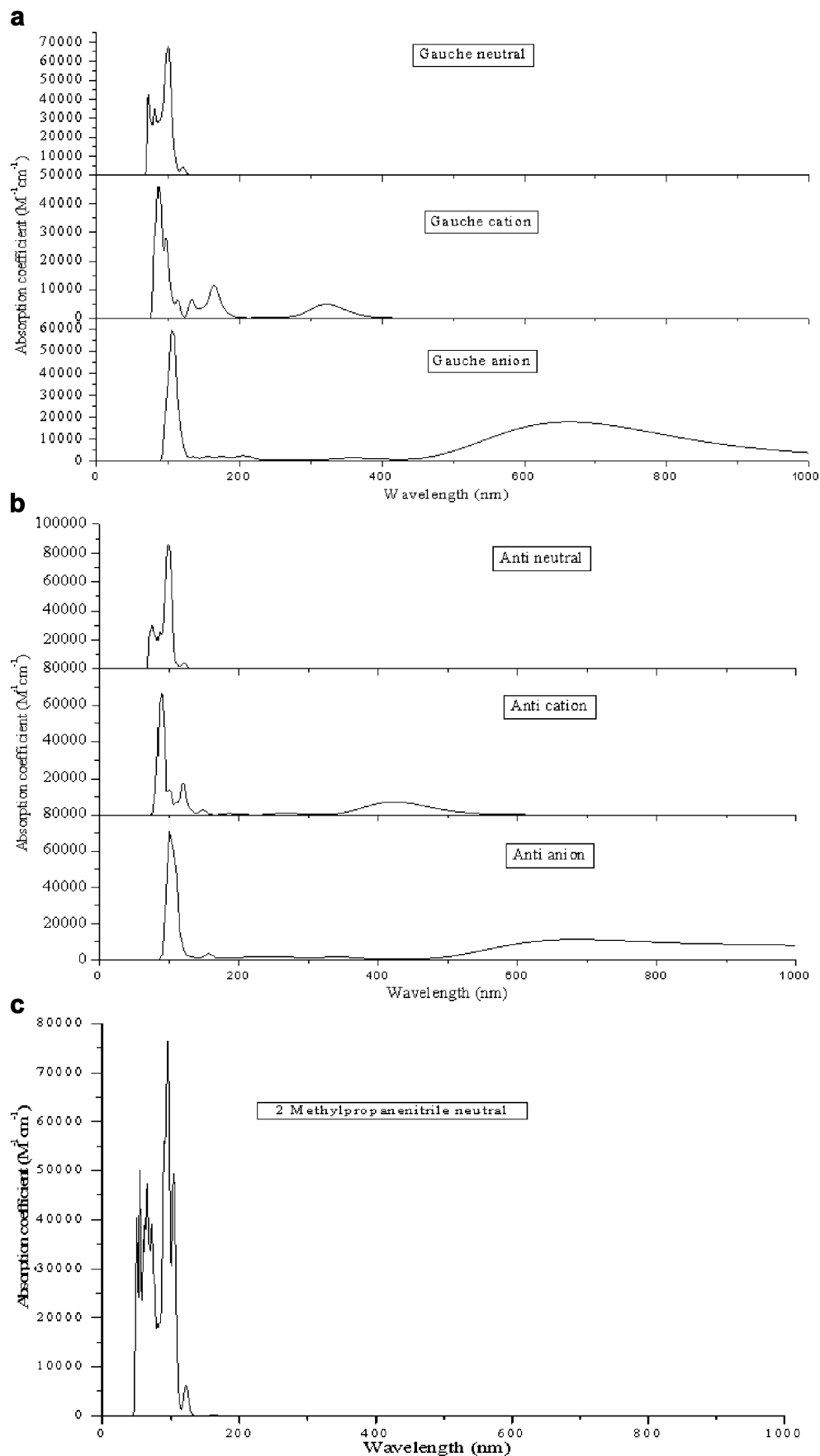
Table 5 Electronic transitions in neutral and ions of gauche and anti conformers n-butyronitrile at MP2/TZVP level theory. H and L represent HOMO and LUMO respectively

Wavelength (nm)	Absorbance (esu^{2}cm^2)	Oscillator strength	Major contribution from transitions	Contribution (%)
Neutral gauche				
73.02	41601	0.1972	H-4→L+12	8
82.3	35059	0.1379	H-6→L+3	9
100.2	67363	0.7742	H→L+2	17
120.76	4092	0.0355	H-1→L	55
Cation				
85.6	45913	0.2683	H-2→L+4	23
95.4	28149	0.2260	H→L+3	22
105.1	7542	0.0637	H-4→L-1	31
132.4	6579	0.1070	H-1→L+1	41
163.9	11396	0.2300	H→L	
322.3	4839	0.1191	H-2→L-1	179
Anion				
106.5	63779	0.2669	H-4→L	33
177.6	1892	0.0311	H→L+14	108
672	17686	0.1552	H→L	130
Neutral anti				
76	29173	0.1792	H-3→L+12	14
86.6	25074	0.3189	H-7→L	21
97.4	84028	0.9308	H-3→L+1	15
118.8	3802	0.0302	H-5→L+5	22
Cation				
87.6	68828	0.3276	H-1→L+5	26
99.7	15232	0.1587	H-10→L-1	18
119.9	19110	0.4500	H-1→L+5	39
436.7	7017	0.1207	H-1→L-1	107
Anion				
100	73994	0.4275	H-4→L+1	48
106.8	62149	0.2160	H-3→L+1	51
156	2623	0.0682	H→L+15	94
635	10456	0.1542	H→L+2	111
Neutral 2 Methylpropanenitrile				
50.4	40538	0.1315	H-10→L+7	11
54.9	49993	0.3547	H-6→L+5	8
60.4	35930	0.1530	H-3→L+19	18
62.9	39988	0.2626	H-9→L+5	20
65.3	47180	0.1769	H-8→L+8	21
72.9	39075	0.2218	H-5→L+8	16
95.8	75848	0.3674	H-3→L+3	22
102.9	49371	0.6613	H→L+2	25
121.8	5885	0.0700	H-1→L	58

The vibrational modes of neutral, cation and anion of anti conformer are summarized in Table 2 and their infrared spectra are shown in Fig. 2b. Cs is the highest symmetry of neutral anti conformer of n-butyronitrile. Upon ionization of neutral anti conformer, C$_1$ becomes its highest symmetry. The most intense mode, the CH$_2$ asymmetric stretching in neutral anti conformer appearing at 3062 cm^{-1} (3.265 μm) does not remain the most intense in its cation and anion. Similar to cation and anion of gauche conformer, the most intense mode is the C≡N

stretching mode in cation and anion of anti conformer. However the IR intensity for this mode in cation and anion of anti conformer is much higher than that in gauche conformer. This mode is more intense in anion than that of cation of anti conformer. The second intense mode in cation of anti conformer is the CH_3 rock appearing at 840 cm^{-1} (11.904 μm). On the other hand for cation of gauche conformer, there are two second intense modes which have the same IR intensity. These modes are the ≡C-C stretching and CH_2 rock modes appearing at 987 cm^{-1} (10.131 μm) and 739 cm^{-1} (13.531 μm) respectively.

On comparing vibrational modes in anion of anti and gauche conformers, all the modes in anion of gauche conformer are intense whereas in anion of anti conformer, the *CH_2 rock, and CH_2 twist are of negligible IR intensity. Similar to gauche conformer, the C≡N stretching mode is blue shifted by 195 and 756 cm^{-1} in cation and anion of anti conformer respectively. The *C-C-C bend, N≡C-C bend, *C-C-C symmetric stretch, CH_3 rock modes are blue shifted in anion and all other modes red shifted than the corresponding modes in neutral anti conformer.

Vibrational frequencies, rotational and distortion constants of neutral 2-methylpropanenitrile isomer of n-butyronitrile at MP2 and CCSD levels are summarized in Table 3 and a comparative spectra of neutral gauche, anti conformer and isomer of butyronitrile is shown in Fig. 2c. The most intense peak observed for neutral 2-methylpropanenitrile isomer is the CH_2 asymmetric stretch appearing at 3069 (3039) cm^{-1} at MP2 (CCSD) level. This mode is also the most intense mode in neutral anti conformer. The second intense mode in neutral 2-methylpropanenitrile isomer is the CH_3 asymmetric stretch which is the most intense mode in neutral gauche conformer of n-butyronitrile.

The rotational and distortion constants for the neutral gauche and anti conformer of butyronitrile at MP2 and CCSD level of theory along with the experimental values are summarized in Table 4. These constants are in good agreement with the available experimental determinations at both MP2 and CCSD level of theory. In all three, gauhe, anti conformer and 2-methylpropanenitrile isomer, the C≡N stretching mode is IR inactive.

Electronic absorption spectra

The electronic absorption spectra of gauche conformer of neutral, cation, and anion of n-butyronitrile is shown in the Fig. 3a. Table 5 gives electronic transitions along with oscillator strength, molecular orbitals involved and their % contribution. The electronic states of gauche and trans conformers of neutral, cation, and anion are ^1A, ^2A, ^2A respectively. There are only α molecular orbitals for neutral
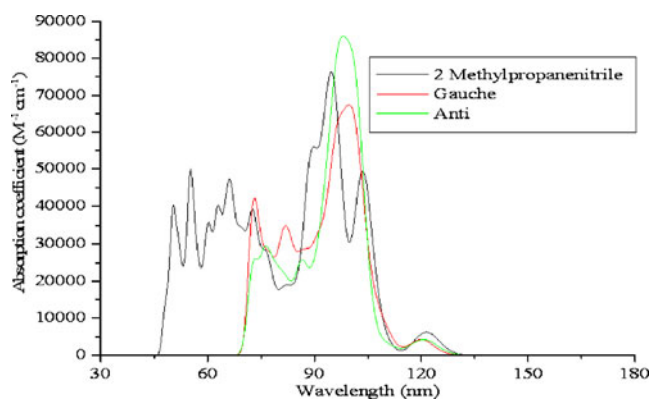

Fig. 4 Comparative electronic absorption spectra of neutral gauche and anti conformer, of n-butyronitrile and its 2 methylpropanenitrile isomer

conformers whereas their ions have both α as well as β molecular orbitals. The electronic absorption spectrum of neutral gauche butyronitrile is characterized by four intense peaks. Out of these four transitions, the first two are in vacuum UV and remaining two peaks in far UV region. These four transitions at 73, 82.3, 100, and 120.7 nm were assigned σ→σ* transitions with major contribution from H-4→L+12, H-6→L+3, H→L+2, and H-1→L transitions respectively. Here H represents highest occupied molecular orbital (HOMO) and L represents lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO gap in neutral gauche conformer is found to be 358.6 kcal mol^{-1}.

The electronic absorption spectrum of cation of gauche conformer shows six intense peaks. These intense peaks appear are at 85.6, 95.4, 105.1, 132.4, 163.9, and 322.3 nm with major contribution from H-2→L+4, H→L+3, H-4→L-1, H-1→L+1, H→L, and H-2→L-1 transitions, respectively. Out of these six transitions the first five transitions are σ→σ* transitions in vacuum and far UV and a remaining transition is the π→π* transition in near UV region. The 387.4 kcal mol^{-1} is the HOMO-LUMO gap for cation of gauche conformer. Electronic absorption spectrum of anion of gauche is characterized by the three intense peaks at 106.5, 177.6, and 672 nm with major contribution from H-4→L, H→L+14, and H-L respectively. The first two transitions are σ→σ* transitions in far UV and third π→π* transition in visible region.

The electronic absorption spectrum of neutral anti conformer and its ions are shown in Fig. 3b. The neutral anti conformer shows four intense peaks. The first three transitions are in vacuum UV region with major contribution from H-3→L+12, H-7→L, and H-3→L+1 at 76, 86.6, and 97.4 nm respectively and a remaining transition is in far UV region with major configuration from H-5→L+5 at 118.8 nm. The HOMO-LUMO gap in neutral anti conformer is 356 kcal mol^{-1}.

The electronic absorption spectrum of cation of anti conformer shows four intense peaks. Two transitions are in vacuum UV, one in far UV and remaining in visible region. First two peaks are at 87.6, 99.7 nm with the major configuration from H-1→L+5 and H-10→L-1, third is at 119.6 nm with major configuration from H-1→L+5 and the last peak is at 436.7 nm with the major configuration from H-1→L-1 respectively. The HOMO-LUMO gap in cation of anti conformer is 387.4 kcal mol^{-1}. The first three transitions are $\sigma \rightarrow \sigma^*$ transitions and remaining transition is $\pi \rightarrow \pi^*$ transition. The electronic absorption spectrum of anion of anti conformer shows four intense peaks are at 100, 106.8, 156, and 635 nm with the major configuration from H-4→L+1, H-3→L+1, H→L+15, and H→L+2 respectively. The HOMO-LUMO gap in anion of anti conformer is 113.6 kcal mol^{-1}. The first three transitions are in far UV with $\sigma \rightarrow \sigma^*$ transitions and remaining transition is $\pi \rightarrow \pi^*$ transition in visible region.

The electronic absorption spectrum of 2-methylpropanenitrile isomer of n-butyronitrile is shown in Fig. 3c where as electronic transitions, and % contribution are summarized in Table 5. The neutral 2-methylpropanenitrile isomer of n-butyronitrile shows nine intense peaks. Out of the nine intense peaks the first seven peaks are in vacuum UV with major configuration H-10→L+7, H-6→L+5, H-3→L+19, H-9→L+5, H-8→L+8, H-5→L+8, and H-3→L+3 at 50.4, 54.9, 60.4, 62.3, 72.9 and 95.8 nm respectively and the remaining two peaks in far UV region with major configuration H→L+2, and H-1→L are at 102.9 and 121.8 nm respectively. The HOMO to LUMO gap for this isomer is 365 kcal mol^{-1}. All the transitions in this neutral isomer are $\sigma \rightarrow \sigma^*$ transitions.

Comparison of electronic absorption spectra

Figure 4 shows the comparative electronic absorption spectrum of neutral gauche and anti conformer and 2-methylpropanenitrile isomer of n-butyronitrile. The electronic absorption spectrum of both neutral gauche and anti conformer shows four intense peaks and isomer shows nine intense peaks. Out of four peaks in neutral gauche conformer, the first two show bathochromic shift of 3 and 4.3 nm than the neutral anti conformer whereas remaining two peaks show hypsochromic shift of 2.8 and 0.1 nm. Neutral gauche butyronitrile exhibits very strong light absorption near 100.2 nm (ε=673636), and weaker absorption at 119 nm (ε=4188), whereas neutral anti conformer exhibits very strong light absorption at 97.4 nm (ε=84028), and weaker absorption at 118.8 nm (ε=3802). Neutral isomer of butyronitrile exhibits very strong light absorption at 95.8 nm (ε=75848) and weaker absorption at 121.8 nm (ε=5885).

Conclusions

We studied infrared and electronic absorption spectra of gauche and anti conformers of neutral, cation, and anion of butyronitrile. Vibrational and electronic absorption spectra of neutral 2-methylpropanenitrile isomer of n-butyronitrile are also studied for comparison. The dipole moment, enthalpy, rotational constants and vibrational frequencies from this work for both the conformers of neutral butyronitrile are in agreement with experimental determinations. The neutral gauche conformer is lower in energy by 0.48 kcal mol^{-1} than the neutral anti conformer at MP2/TZVP level. Large change in infrared spectra of neutral gauche and anti conformer of n-butyronitrile upon ionization is observed. Number of intense peaks is more in anion than that of cation for gauche as well as anti conformer. It is observed that the C≡N stretching mode is of very weak intensity in neutral anti and gauche conformers as well as 2-methylpropanenitrile isomer. However this mode becomes the most intense in cation and anion of anti as well as gauche conformer of n-butyronitrile. The electronic absorption spectrum of neutral anti and gauche conformers is characterized by four intense peaks whereas that of neutral 2 methylpropanenitrile isomer is characterized by nine intense peaks. All the transitions in gauche and anti conformer of neutral are $\sigma \rightarrow \sigma^*$ transitions and their ions show $\sigma \rightarrow \sigma^*$ as well as $\pi \rightarrow \pi^*$ transitions. This study should provide useful guidelines for detecting and identifying conformers of n-butyronitrile, their ions and its isomer in different astrophysical environment.

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