



Spectral Investigations of Protonated Naphthalene using Density Functional Theory

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ABSTRACT

We have done the spectral investigations of protonated naphthalene (NpH^+) theoretically. The optimized molecular geometry, structural parameters, harmonic frequencies, atomic charges, dipole moment and several thermodynamic functions of protonated naphthalene (NpH^+) have been calculated using the Becke three-parameter Lee-Yang-Parr functional (B3LYP) and 6-311++G(d,p) basis set. The calculated vibrational wave numbers of protonated naphthalene have been systematically analyzed and assigned to different normal modes of the molecules.

Keywords: DFT methods; Molecular geometries; Protonated naphthalene; Vibrational assignment

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) which occur in coal, crude oil, and gasoline are interesting targets of studied in connection with astrophysics of interstellar medium being responsible for infrared emission [1-4]. Polycyclic aromatic hydrocarbons also carry certain unidentified absorption features in spectra of starlight due to intervening interstellar material [5,6]. However many aromatic species are present in cationic state. [7,8]. PAH cation can be Open-shell species, such as the cations of commercially available PAHs (e.g. naphthalene) or closed-shell species, which are cations of PAH radicals. One class of closed-shell aromatic cations may be described as protonated PAHs. Protonated aromatic hydrocarbon molecules (H^+PAH) are of high spectroscopic interest. They occur as intermediates in electrophilic aromatic substitution reactions [9] which can be considered as one of the most fundamental reaction mechanisms of aromatic molecules [10]. H^+ PAH ions are also considered to be present in the interstellar medium and invoked as possible carriers of the unidentified infrared emission (UIR) bands and the diffuse interstellar bands (DIB) [11-17]. Protonated aromatic hydrocarbon molecules constitute an important family of organic molecules. They are present in many reactive systems, e.g., combustion [18], plasma decontamination reactors [19], and exhaust of airplane engines [20]. Naphthalene (Np) is with the formula C_{10}H_8 is the building block of PAH. The spectral investigation of protonated naphthalene (NpH^+) is fundamental in understanding the UIR emission in ISM. In particular, the photo dissociation spectrum of NpH^+ by Alata et al. represents the first observation of vibrationally resolved electronic absorption spectra of NpH^+ in the gas phase [15]. The experiment utilized a discharge source for ion production and detection of the neutral photo fragments. Alexander et al presented the electronic photodissociation spectrum of the $\text{S}_1 \leftarrow \text{S}_0$ transition of the NpH^+-Ar complex [21].

In this paper we have calculated the optimized molecular geometry, structural parameters, harmonic frequencies, atomic charges, dipole moment and several thermodynamic functions of protonated naphthalene (NpH^+) using the Becke three-parameter Lee-Yang-Parr functional (B3LYP) and 6-311++G(d,p) basis set. The calculated vibrational wave numbers in FTIR and Raman spectra of protonated naphthalene have been systematically analyzed and assigned to different normal modes of the molecules.

COMPUTATIONAL METHOD

Three distinct protonation sites on naphthalene are possible, as shown in Figure 1. Density functional theory (DFT) calculations were performed for all the three isomers of Protonated Naphthalene α -NpH⁺, β -NpH⁺ and γ -NpH⁺ to calculate the optimized molecular energies, zero point vibrational energies, dipole moments and thermodynamic functions using the Gaussian 03 software package [22] and Gaussian type basis functions. The geometries of NpH⁺ conformers were optimized by minimizing the energies with respect to all geometrical parameters without imposing any constraint. Molecular structure optimization of the α -NpH⁺, β -NpH⁺ and γ -NpH⁺ have been done using B3LYP methods with 6-311++G(d,p) basis sets. The stability of the optimized geometries was confirmed by wave number calculations, because values of all the wave numbers are positive. Assignments of the normal mode of vibrational frequencies were made by visual inspection of individual mode using Gaussian view software.

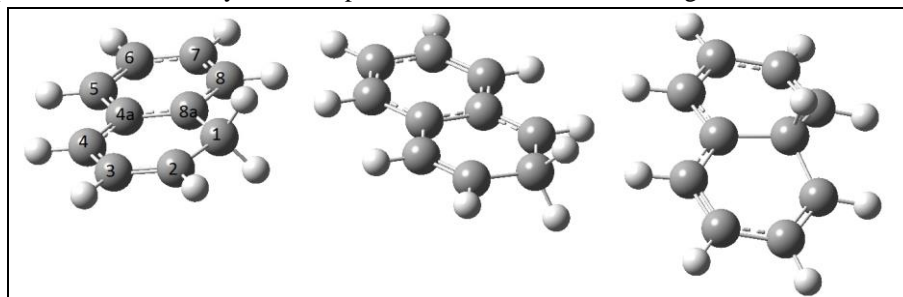


Figure 1: Optimized structures of the three stable isomers α -NpH⁺, β -NpH⁺ and γ -NpH⁺ with employed atom numbering at B3LYP/6-311++G(d,p)

RESULTS AND DISCUSSION

Molecular geometry

The calculated optimized molecular energies, zero point vibrational energies, dipole moments and thermodynamic functions using B3LYP method with 6-311++G(d,p) basis sets for all the three isomers of Protonated Naphthalene α -NpH⁺, β -NpH⁺ and γ -NpH⁺ are shown in Table 1. As the total optimized energy is lowest for α -NpH⁺, it will be the most stable isomer. The dipole moment of γ -NpH⁺ is least and that of β -NpH⁺ is largest, therefore β -NpH⁺ is more polar than any other conformer.

To calculate structural parameters, APT charges at various atomic sites, fundamental vibrational wave numbers along with their corresponding intensities in IR spectrum, Raman activities and assignments of the normal mode of vibrational frequencies we have used the α -NpH⁺ conformer using B3LYP method and 6-311++G(d,p) basis sets.

The calculated bond lengths and bond angles for α -NpH⁺ using B3LYP method and 6-311++G(d,p) basis set are reported along with the corresponding experimental values [21] in Table 2. We see that the experimental values of bond lengths and bond angles for α -NpH⁺ are very close to calculated bond lengths and bond angles using B3LYP method and 6-311++G(d,p) basis set.

The APT (atomic polarizability tensor) charges at various atomic sites of protonated naphthalene α -NpH⁺ and naphthalene Np molecules calculated using B3LYP method and 6-311++G(d,p) basis set are shown in Table 3. We see the magnitudes of charges decrease at the C1, C6-C8 sites increase in going from the naphthalene to protonated naphthalene molecules. The ATP charges of C2-C5 change its sign in going from the naphthalene to protonated naphthalene molecules.

Table 1: Calculated energies, dipole moment, zero-point Vibrational energies and thermodynamic functions of the three stable NpH⁺ isomers at B3LYP/6-311++G (d,p)

S.No.	Species	Total energies E(hartree)	Zero-point Vibrational energy(J/mol)	Dipole moment (Debye)	Constant volume molar heat capacity(C _v) (cal/mol K)	Entropy S(cal/mol K)
1	α	-386.54779	408429.5	0.5448	31.144	86.98
2	β	-386.53992	407810.8	0.7895	31.234	86.298
3	γ	-386.50814	405430.1	0.2209	31.339	86.165

Table 2: Bond lengths (angstroms) and bond angles (degrees) of nicotinic acid and 6-fluoronicotinic acid compared with experimental data [Ref. 21] of α -NpH⁺

Parameters	Experimental	Calculated B3LYP/6-311++G(d,p)
Bond Length		
C1-C2	1.469	1.497
C2-C3	1.371	1.37
C3-C4	1.409	1.405
C4-C4a	1.405	1.435
C4a-C5	1.419	1.413
C5-C6	1.379	1.358
C6-C7	1.409	1.398
C7-C8	1.394	1.394
C8-C8a	1.393	1.394
C4a-C8a	1.428	1.419
C8a-C1	1.486	1.515
Bond Angles		
C8a-C1-C2	117	114.6
C1-C2-C3	121.9	122
C2-C3-C4	119.3	121.7
C3-C4-C4a	123.4	121
C4-C4a-C8a	119	119.9
C4a-C8a-C1	119.3	120.5
C8a-C4a-C5	120.6	118.7
C4a-C5-C6	119.5	121.2
C5-C6-C7	119.7	119.8
C6-C7-C8	121.5	119.7
C7-C8-C8a	119.9	121.4
C8-C8a-C4a	118.8	119.3

Table 3: APT Charges at various atomic sites for protonated naphthalene molecules (α -NpH⁺) and Naphthalene Molecule using B3LYP/6-311++G(d,p)

Atoms	Protonated Naphthalene(NpH ⁺)	Naphthalene (Np)
C1	-0.895	-0.238
C2	0.08	-0.124
C3	-0.364	0.143
C4	-0.17	0.143
C5	0.079	-0.124
C6	-0.322	-0.238
C7	-0.215	-0.124
C8	-0.127	-0.124
C4a	0.416	
C8a	0.113	

Vibrational assignments

The maximum number of potentially active vibrational modes of a nonlinear molecule which contain N atom is equal to (3N-6). Apart from these there will be three translational and three rotational degrees of freedom [23]. Hence α -NpH⁺ molecule which has 19 atoms will have 51 normal modes of vibration, considered under C_s point group symmetry. For N-atomic molecules, 2N-3 of its vibrations will be planer and N-3 will be non-planer [24]. Thus, with respect to the reflection on the symmetry plane, 35 of these modes will be planar (A') and 16 will be non planar (A''). The 51 normal modes of vibrations are distributed amongst the symmetry species as $\Gamma_{\text{vib}}=36A'+16A''$. The detailed analysis of fundamental modes of vibrations frequencies, Raman intensity, Raman activity and vibrational assignments of α -NpH⁺ using B3LYP method with 6-311++G(d,p) basis set are listed in Table 4. When the vibrational assignments of α -NpH⁺ are compared with the assignments of the naphthalene [25], we see that three additional mode appears at 2954 cm⁻¹, 2953 cm⁻¹ and 82 cm⁻¹ due to addition of H atom. Almost all other assignments are same as reported earlier [25].

Table 4: Calculated vibrational frequencies (cm⁻¹), IR Intensity (KM/Mole), Raman activity (A⁴amu⁻¹) of α - NpH⁺ and their Vibrational Assignments

Protonated naphthalene at B3LYP/6-311++G(d,p)			Approximate description of vibration ^a
Wave Numbers	IR Intensity	Raman Activity	
3187	16	355	CH-str. (+)
3183	28	179	CH-str. (-)
3173	29	76	CH-str. (-)
3171	10	130	CH-str.
3159	1	84	CH-str.
3153	4	79	CH-str.
3149	10	51	CH-str.
2954	31	235	CH ₂ sym.str.
2953	13	128	CH ₂ asym.str.
1626	0	165	C=C str.
1597	0	62	C=C str.
1556	1	84	C=C str. (+)
1514	7	3	C=C str.
1471	6	4	CC str.; CH bend
1445	7	27	CH ₂ -bend
1438	1	27	CC str.; CH bend
1393	0	19	CC str.; CH bend
1356	0	13	CH-bend.; CC str
1310	4	66	CC str.; ring def.
1277	3	17	CC str.; CH bend
1233	0	54	CH-bend (-); CC str.
1202	1	19	CC str.; CH bend
1202	0	4	CH-bend (-); CC str.
1179	0	8	CC str.; CH bend
1175	0	19	CH-bend
1139	1	4	CH-bend.; CC str.
1092	2	8	CH-bend
1055	3	19	CC str.
984	0	4	CC str.
964	0	10	CH-wagg. (-)
961	2	44	CH-wagg. (-)
954	10	0	CH-wagg.
931	2	0	CH-wagg.
920	0	0	CCC bend; ring def.
870	0	0	CH-wagg.
794	22	1	CH-wagg.
794	0	4	CCC bend; ring def.
751	58	0	CH-wagg (+)
747	0	0	CC-t
713	9	2	Breathing
660	30	0	CH-wagg.
612	0	31	CCC bend. in two rings (-)
542	1	0	CC-t
506	0	0	CCC bend. in two rings (+)
485	0	0	CCC bend.
469	2	0	CC-t; ring def.
429	7	9	CC-t; ring def.
357	0	15	CC-t
247	6	0	Envelope flap
171	0	0	TTR
82	0	0	Butterfly

^aSymbols: TTR, Torsion of two rings against each other; Bend: Bending; def.: deformation; t:torsion; str.: stretching; wagg: Wagging; vib:vibration; (-):out-of-phase;(+) in phase, sym: symmetric, asym: antisymmetric.

CONCLUSION

In the present paper, attempt has been made for the proper vibrational assignments of protonated naphthalene α -NpH⁺. The assignments are similar to naphthalene except three modes at frequencies 82 cm⁻¹, 2953 cm⁻¹, 2954 cm⁻¹. The optimized geometry, harmonic vibrational wave numbers and intensity of α -NpH⁺ have been calculated by B3LYP functional employing basis sets up to 6-311++G (d,p). In most cases the calculated bond lengths and bond angles are found very close to the reported experimentally.

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