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Density functional theory studies on the structure and vibrational assignments of 2-hydroxy-4-methyl-5-nitropyridine

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ABSTRACT
In this study, the solid phase FT-IR and FT-Raman spectra of the 2-hydroxy-4-methyl-5-nitropyridine (HM5NP) was recorded in the range 4000–400 cm^{-1} and 3500–100 cm^{-1}, respectively. Theoretical information on the optimized geometry, harmonic vibrational frequencies, Infrared and Raman intensities were obtained by means of density functional theory (DFT) using standard B3LYP/6-311++G** level. This information was used in the assignment of the various fundamentals. Comparison of the simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes.

Introduction

Pyridine and its derivatives are very important in industrial field as well as in biochemistry. Some pyridine system is active in the metabolism in the body. They can be the parent compound of many drugs, including the barbiturates. Pyridine and its derivatives are used as solvents and starting material for the synthesis of target compounds such as insecticides, herbicides, medicines, vitamins, food flavorings, feed additives, dyes, rubber chemicals, explosives, disinfectants, and adhesives. Pyridine is also used as a denaturant for antifreeze mixtures, as a dyeing assistant in textiles and in fungicides. Pyridine derivatives have been extensively studied from the spectroscopic point of view, due in part to its presence in many chemical structures of high interest in a variety of biomedical and industrial fields. The vibrational spectra of substituted pyridine have been the subject of several investigations [1-3]. Consideration of all these factors lead to undertaking detail Infrared Raman spectral studies and vibrational assignments in 2-hydroxy-4-methyl-5- nitro pyridine (HM5NP).

Accurate vibrational assignments for compound are necessary for characterization of materials. The vibrational assignments at the compounds can be proposed on the basis of wave number agreement between computer harmonics and observed fundamental. The density functional theory has proven to be an essential tool for interpretation and predicting vibrational spectra [4, 5].

Experimental Details

The compound HM5NP was purchased from Lancaster Chemical Company USA, with a stated purity of 99% and it was used as such without further purification. The FT-Raman spectrum of HM5NP was recorded using 1064nm line of Nd:YAG laser as excitation wave length in the region 3500–100cm^{-1} on thermo electron corporation model Nexus 670 spectrometer equipped with FT-Raman module accessory. The FT-IR spectrum of the title compound was recorded in the region 4000–400cm^{-1} on Perkin Elmer Spectrophotometer in KBr pellet. The spectrum was recorded at room temperature with a scanning speed of 30 cm^{-1}min^{-1} and the spectral width of 2.0 cm^{-1}. The observed experimental FT-IR and FT-Raman spectra and theoretically predicted IR and Raman spectra at DFT and B3LYP levels are shown in Fig .1 and 2, respectively.

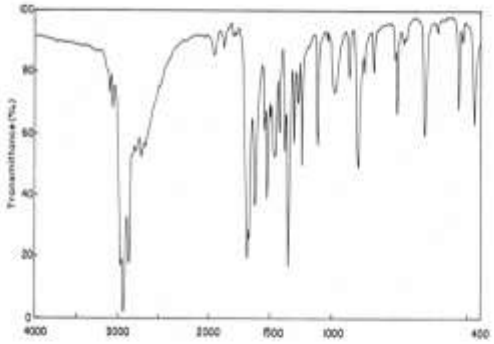

Fig. 1 FT-IR spectrum of 2-hydroxy-4-methyl-5-nitropyridine

Computational methods

All the calculations were performed using the 3-parameter hybrid functional (B3) for exchange part and the Lee-Yang-Parr (LYP) correlation function, with 6-311++G** as the basis set using the Gaussian 09 suite of program [6]. The basis set 6-311++G** is a triple–split valance basis set that increases the flexibility of the valence electrons.

It is useful for the most studies involving medium–size system [7]. DFT calculations were reported to provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlations, for basis set deficiencies, and for anharmonicity.

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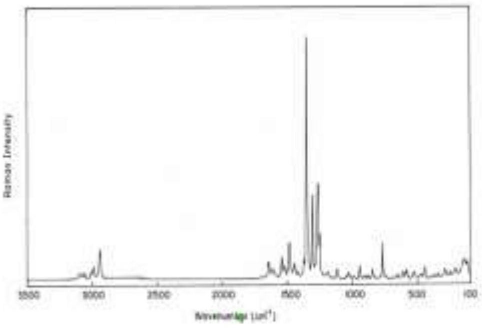

Fig. 2 FT-IR spectrum of 2-hydroxy-4-methyl-5-nitropyridine

A number of studies have been carried out regarding the calculations of vibrational spectra using B3LYP methods with the 6-311++G** basis set. As a result, it was found that the experimental vibrational frequencies and IR intensities could be reported very accurately. The scaling factor was applied successfully to the B3LYP [8, 9] method and found to be easily transferable to a number of molecules. Thus vibrational frequencies calculated using the B3LYP function with 6-311++G** as the basis set can be utilized to eliminate the uncertainties in the fundamental assignment in the IR spectra.

The vibrational modes were assigned by means of visual inspection using the GAUSS VIEW program [9]. The analysis for the vibrational modes of HM5NP is presented in some detail in order to better describe the basis for the assignments. From the basic theory of Raman scattering Raman activities (S_i) calculated by Gaussian 09 program have been converted to relative Raman intensities (Ii) using the following relationship:

$$I_i = \frac{f(\nu_o - \nu_i)^4 \, S_i}{\nu_i\left[1-exp\left(\frac{-hc\nu_i}{KT}\right)\right]} \qquad (1)$$

Where ν_o is the exciting wave number (in cm $^{-1}$ units), ν_i is the vibrational wave number of the in i^{th} normal mode, h, c, and k are universal constant and f is the suitably chosen common scaling factor for all the peak intensities.

Result and Discussion

Geometrical Structure

The molecular structure of HM5NP having C_s point group symmetry. The most optimized geometry is performed at B3LYP/6-311++G** basis set of HM5NP molecule with atoms numbering scheme shown in Fig.3. The optimized bond length and bond angles of the title compound which are calculated using DFT (B3LYP) method with 6-311++ G** basis set are shown in Table.1. The optimized structure of the title compound was compared with other similar systems for which the crystal structures have been solved [10]. From theoretical values we can find that most of the optimized bond lengths and bond angles are slightly longer and shorter than the experimental values. These variations are due to the substitution of the methyl, nitro and hydroxyl groups.

Assignments of spectra

A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 58 standard internal coordinates containing 13 redundancies were defined as given in Table.2. From these, a non-redundant set of local symmetry coordinates was construed by suitable linear combinations of internal coordinates following the recommendation of Pulay *et al.* [11] and they are presented in Table.3. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

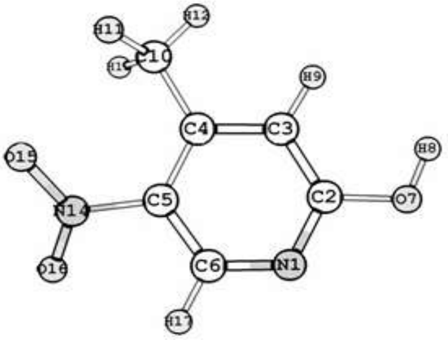

Fig. 3 Molecular structure of 2-hydroxy-4-methyl-5-nitro pyridine

The observed and calculated wave numbers and normal mode descriptions for the title compound are reported in Table.4. When using computational methods to predict theoretical normal vibrations for relatively complex polyatomic, scaling strategies are used bring computed wave numbers. For the DFT method employed in this work the simplest limiting scaling strategy was used.

In order to reproduce the observed wave numbers, refinement of scaling factors were applied and optimized via least-square refinement algorithm which resulted is an average difference between the experimental and SQM wave numbers for 6-311++G** basis set. The vibrational assignments in the present work are based on the DFT/6-311++G** frequencies, Infrared intensities, Raman activities as well as characteristic group frequencies. The 45 normal modes of HM5NP are distributed among the symmetry species as √vib=31A'(in-plane)+14A" (out-of-plane). The detailed vibrational assignments of fundamental modes of HM5NP have been reported in Table.4. Assignments were made through visualization of the atomic displacement representations for each vibration, viewed through GAUSSVIEW [9] and matching the predicted normal wave numbers and intensities with experimental data. It is convenient to discuss the vibrational spectra of HM5NP in terms of characteristic spectral regions as described below:

O–H vibrations

The O–H stretching vibrations normally appear around 3600 cm^{-1} as in, for phenol [12]. The band values observed at 3452 cm^{-1} in infrared spectrum and 3456 cm^{-1} in FT-Raman spectrum are assigned to O–H stretching vibration in HM5NP. The O-H in-plane and out-of-plane bending vibrations calculated at 1438 cm^{-1} and 733 cm^{-1}, respectively. These vibrations show good agreement with recorded spectral values and literature [13, 14].

C–H vibration

The hetero aromatic organic compounds and its derivatives are structurally very close to benzene and commonly exhibit multiple week bands in the region 3100–3000 cm^{-1} due to C–H stretching vibrations [13]. In the title molecule, the computed values at 3191, 3152 cm^{-1} in HM5NP at B3LYP/6-311++G ** method are assigned to C–H stretching vibrations. These assignments are in line with the literature and further in this region, the bands not much affected due to the nature and position of the substitution. The C–H in-plane bending vibrations normally occur as a number of strong to week intensity sharp bands in the region 1300–1000 cm^{-1} [14, 15]. The bands for C–H in-plane bending vibrations are calculated at

1309, and 1171 cm^{-1} and these are in good agreement with recorded values at 1313 cm^{-1} in infrared spectrum and 1314, 1176 cm^{-1} in Raman spectrum. The out-of-plane bending vibrations are found at 982, 829 cm^{-1}. This assignment is also supported by the literature as well as recorded spectra [14, 15].

CH3 vibration

The C–H methyl group stretching vibrations are highly localized and generally observed in the range 3000–2800 cm^{-1} [16, 17]. In the present investigation, the bands with sharp peaks are found at 3107, 2960 and 2956 cm^{-1} are assigned to CH3 asymmetric and symmetric stretching vibrations. These values are in good agreement with the calculated values. The bands found at 1491, 1454, and 1411 cm^{-1} are assigned to CH3 in-plane, out-of-plane and bending vibrations, respectively. The computed values identified at 1325 and 1020 cm^{-1} are assigned to CH3 in-plane rock and out-of-plane rock modes of HM5NP molecule. The computed values at 225 cm^{-1} is assigned to CH3 twisting vibration of HM5NP molecule. This assignment is also supported by the literature [18].

C□C and C□CH3 vibration

The ring stretching vibrations (C–C) are very much prominent in the spectrum of pyridine and its derivatives are highly characteristic region of the hetero aromatic ring itself [18]. The (C═C) stretching modes are normally observed in the range 1650–1400 cm^{-1} in benzene derivatives [15]. In the present molecule, the values found at 1626, 1595, 1462, 1356, and 762 cm^{-1} are assigned to C–C stretching vibrations. The band identified at C4 is much affected by the substitution of the methyl group because of this reason it shows the lower stretching vibration in title molecule. The band observed at 763 cm^{-1} in FT-IR spectrum and 766, 325 cm^{-1} in FT-Raman spectrum are assigned to C–CH3 in-plane and out-of-plane bending vibrations, respectively. These assignments are in line with the literature and further in this region, the bands much affected due to the nature and position of the substitution.

In the present work, the computed values are 612, 590, and 362 cm^{-1} are assigned C–C–C in-plane bending vibrations. The bands identified at 432, 191, and 120 cm^{-1} is assigned to C–C–C out-of-plane bending vibrations. The in-plane bending vibrations are slightly below the expected range. This is due to the replacement of C by N. These assignments are in line with the literature [19-21].

C–N and C–NO2 vibrations

The pyridine absorbs strongly in the region 1600–1500 cm^{-1} due to C═N ring stretching vibrations [13]. Accordingly, the observed values are identified at 1201, 1104 and 1047 cm^{-1} in IR and Raman spectra, respectively. These bands have strong intensity and these are lower than the expected value. The strong intensity of the band may due to the mixing of C═N with C═C, both occurring at the same frequency. The C–N stretching vibrations are always mixed with other bands and normally occur in the region 1266–1382 cm^{-1} [22-24]. The band observed at 375 cm^{-1} in FT-Raman spectrum and computed value at 374 cm^{-1} in B3LYP /6-311++G ** method are assigned to C—NO$_2$ in-plane vibration. The calculated value found at 209 cm–1 is assigned to C—NO$_2$ out-of-plane vibration, which is in close agreement with the literature value.

NO2 vibration

Aromatic nitro compounds have strong absorptions due to the asymmetric and symmetric vibrations of the NO$_2$ group at 1570–1485 and 1370–1320 cm^{-1}, respectively. Hydrogen bonding has little effect on the NO$_2$ asymmetric stretching vibration [25, 26]. The computed values at 1547 cm^{-1} and 1276 cm^{-1} are assigned to NO$_2$ asymmetric and symmetric stretching vibrations, respectively. The calculated value found at 853 cm^{-1} is assigned to scissoring vibration. The other vibrations such as wagging, rocking and twisting are presented in Table.4. All these vibrations show good agreement with computed harmonic frequency as well as recorded spectral data.

C–O vibrations

The C–O stretching generally occurs as a strong absorption in the region from 1260–1000 cm^{-1} [27]. The theoretically computed value is found at 971 cm–1 is assigned to C–O stretching vibration. This value is slightly below the expected value due to the nature and position of the substituent of the methyl and hydroxyl groups. The computed values at 719 cm^{-1} and 510 cm^{-1} are assigned to C–O in-plane and out-of-plane bending vibrations of HM5NP molecule. These assignments are also supported by the literature.

Computed IR intensity and Raman activity analysis

Computed vibrational spectral IR intensities and Raman activities of the corresponding wave numbers by DFT/6-311++G** basis set have been collected in the Table.5. Comparison of the IR intensities and Raman activities calculated by DFT/6-311++G** level with experimental values exposes the variation of IR intensities and Raman activities. These variations may due to the substitution of the hydroxyl, methyl and nitro group atoms.

Vibrational force constant

The output files of the quantum mechanical calculations contain the force constant matrix in Cartesian coordinates and in Hartree/ Bohr2 units. These force constants were transformed to the force fields in the internal local-symmetry coordinates. The force field determined was used to calculate the vibrational potential energy distribution among the normal coordinate. In the title molecule the values show the variation due to the substitution of the hydroxyl, methyl and nitro groups. They are listed in Table.5.

Conclusion

The DFT–based SQM approach provides the most reliable theoretical information on the vibrational properties of medium sized molecules. Based on the force field obtained by DFT calculations at B3LYP/6-311G** level, the vibrational wave numbers, infrared intensities and Raman activities were calculated and a complete vibrational analysis of the title compound has been carried out. The predicted harmonic and anharmonic frequencies were compared with the experimental data. As one can notice that, there is a very good agreement between the experimental vibrational wave numbers and theoretically determined values.

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Table 1 Geometrical parameters of HM5NP

Bond length	value(Å)		Bond angle	value(Å)	
	Cal	Expt[a]		Cal	Expt[a]
N1-C2	1.33	1.34	C2-N1-C6	117	117
N1-C6	1.33	1.34	N1-C2-C3	124	123
C2-C3	1.40	1.40	N1-C2-O7	114	
C2-O7	1.35		C3-C2-O7	122	118
C3-C4	1.39		C2-C3-C4	120	119
C3(5)-N9(14)	1.47		C2(4)-C3(5)-N9(14)	123	
C4-C5	1.41		C4(6)-C3(5)-N9(14)	117	
C5-C6	1.40	1.40	C3-C4-C5	115	119
C5(3)-H16(9)	1.08	1.08	C3-C4-C12	119	
C6-H17	1.08		C5-C4-C12(10)	120	
O7-H8	0.96		C4-C5-C6	125	118
N9(14)-O10(15)	1.23		C4(2)-C5(3)-H16(9)	120	
N9(14)-O11(16)	1.23		C6(4)-C5(3)-H16(9)	119	
C12(10)-H13(11)	1.09		N1-C6-C5	124	123
C12(10)-H14(12)	1.09		N1-C6-H17	117	
C12(10)-H15(13)	1.09		C5-C6-H17	119	120
			C2-O7-H8	110	
			C3(5)-N9(14)-O10(15)	118	
			C3(5)-N9(14)-O11(15)	118	
			O10(15)-N9(14)-O11(16)	124	
			C4(11)-C12(10)-H13(11)	111	
			C4(11)-C12(10)-H14(12)	110	
			C4-C12-H15	112	
			H13-C12-H14	109	
			H13-C12-H15	106	
			H14-C12-H15	109	

[a]Taken from Ref.[10]

Table 2 Definition of internal coordinates of HM5NP

No.	Symbol	Type	Definition
Stretching			
1-4	Ri	CC aromatic	C2-C3,C3-C4,C4-C5,C5-C6
5	Ri	CC methyl	C4-C9
6-7	Pi	CN aromatic	C2-N1,C6-N1
8	Pi	CN nitro	C5-N14
9-10	Qi	CH aromatic	C3-H9,C6-H17
11-13	Ri	CH methyl	C10-H11,C10-H12,C10-H13
14-15	Pi	NO	N14-O15,N14-O16
16	Qi	CO	C2-O7
17	Qi	OH	O7-H8
In-plane bending			
18-23	αi	Ring	N1-C2-C3,C2-C3-C4,C3-C4-C5,C4-C5-C6,C5-C6-N1,C6-N1-C2
24-27	βi	CH	C2-C3-H9,C4-C3-H9,C5-C6-H17,N1-C6-H17
28-29	βi	CN nitro	C5-N14-O15,C5-N14-O16
30	βi	NO	O15-N14-O16
31-32	βi	bCN	C6-C5-N14,C4-C5-N14
33-34	βi	bCC	C3-C4-C10,C5-C4-C10
35-37	ωi	CCH methyl	C4-C10-H11,C4-C10-H12,C4-C10-H13
38-40	ωi	HCH	H11-C10-H12,H12-C10-H13,H11-C10-H13
41-42	ωi	bCO	N1-C2-O7,C3-C2-O7
43	ωi	bOH	C2-O7-H8
Out-of-plane bending			
44-45	ωi	wCH	H9-C3-C4-C2,H17-C6-N1-C5
46	ωi	CN	C5-N14-O15-O16
47	ωi	CH	C5(C3)-C4-C10-H11(H12,H13)
48	ωi	wCN	N14-C5-C6-C4
49	ωi	wCC	C10-C4-C5-C3
50	ωi	wCO	N1-C2-O7-C3
51-52	ωi	wOH	N1-C2-O7-H8,C3-C2-O7-H8
53-58	ti	Ring	N1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,C4-C5-C6-N1, C5-C6-N1-C2,C6-N1-C2-C3

Table 2: Symmetry coordinates of HM5NP

No	Type	Definition
Stretching		
1-4	CC aromatic	R1,R2,R3.R4
5	CC methyl	R5
6-7	CN aromatic	P6,P7
8	CN nitro	P8
9-10	CH aromatic	Q9,Q10
11	CH $_3$ss	(R11+R12+R13)/√3
12	CH$_3$ ips	(2R11-R12-R13)/√6
13	CH$_3$ ops	(R12-R13)/√2
14	NO$_2$ ss	(P14-P15)/√2
15	NO$_2$as	(P14+P15)/√2
16	CO	Q16
17	OH	Q17
In-plane bending		
18	Rtrig	(α18-α19+α20-α21+α22-α23)/√6
19	Rsym	(-α18-α19+2α20-α21-α22+2α23)/√12
20	Rasy	(α18-α19+α21+α22)/2
21-22	bCH	(β24- β25))/√2, (β26- β27))/√2,
23	NO$_2$ rock	(β28- β29))/√2
24	NO$_2$ twist	(β28+ β29))/√2
25	NO$_2$ sciss	(2β30-β28- β29))/√6
26	bCN	(β31- β32))/√2
27	bCC	(β33- β34))/√2
28	CH$_3$ sb	(-ω35- ω36- ω37+ ω38+ ω39+ ω40)/√6
29	CH$_3$ ipb	(-ω38- ω39+2 ω40)/√6
30	CH$_3$ opb	(ω38- ω39)/√2
31	CH$_3$ ipr	(2ω35- ω36- ω37)/√6
32	CH$_3$ opr	(ω36- ω37)/√2
33	bCO	(ω41- ω42)/√2
34	bOH	ω43
Out-of-plane		
35-36	wCH	ω44, ω45
37	NO$_2$ wagg	ω46
38	CH$_3$ twist	ω47
39	wCN	ω48
40	wCC	ω49
41	wCO	ω50
42	wOH	(ω51- ω52)/√2
43	Rtrig	(t53-t54+t55-t56+t57-t58)/√6
44	Rsym	(t53-t55+t56-t58)/2
45	Rasy	(-t53+2t54-t55-t56+2t57-t58)/√12

Table 4 Vibrational assignments of HM5NP

S.No.	Observed frequency		Unscaled	Scaled	Vibrational Assignments
	FT-IR	FT-Raman			
1	3452	3456	3831	3455	95νOH
2		3190	3198	3191	89νCH
3		3157	3165	3152	86νCH
4		3107	3123	3104	82νCH_3 asym.
5		2960	3113	2968	88νCH_3 asym.
6	2955	2956	3050	2958	85νCH_3 sym.
7		1635	1640	1626	75νCC+20νOH+12 νNO_2
8	1604	1601	1610	1595	68νCC+21νCH+15νCN
9	1542	1543	1569	1547	65νNO_2+25 νCN+15δCH
10		1487	1516	1491	82δCH_3 ipb+10δCO
11		1463	1489	1462	62νCC+20δCH+12νCN asym.
12	1457	1455	1474	1454	85 γCH_3 opb
13	1437		1421	1438	72δOH ipb+22CO+13νCC
14	1409	1403	1419	1411	76δCH_3 sym+12δOH
15	1349	1345	1368	1356	58νCC+ 20νCC + 12δCH
16		1332	1356	1325	42δCH_3ipr+25δOH+18δCH +12δCC
17	1313	1314	1328	1309	75 δCH +20νCC
18	1280		1293	1276	65νNO_2+21νCC+ 12νCN
19		1201	1212	1202	42νCN+22δOH+18νCN
20		1176	1182	1171	74δCH+22νCN
21		1104	1115	1103	42νC-NO_2+25δCH_3 ipb+12δRing
22	1047		1054	1041	42νCN+25νCN+20δCH_3 ipr
23	1022		1037	1020	72 γCH_3 opr+12 γCH
24		980	980	982	75γCH+12γCH+10γRing
25	971		971	971	48νCO+28δCH_3 ipr+18δRing
26	852		858	853	65δNO_2 sciss+25δRing+12δCH
27	832	835	846	829	74γCH+15γCH+10γRing
28	763	766	772	762	52νC-CH_3+35δRing
29	731	734	763	733	65γOH+18γCN+10γCH
30	725		733	719	42δ CO+21δC-NO_2+18γ C-CH_3opr
31	640	643	655	645	55δNO_2wagg+30γOH+10γCH
32	611	615	609	612	61δRing+20νCN+12 νCO
33	593		572	590	64δRing+20δC-CH_3+12δCH
34	509	509	531	510	51γCO+28δC-CH_3 ipr+12δCN
35	465		479	465	53δC-CH_3+22δRing
36	430		448	432	64γRing+20γC-CH_3+12γCH
37		375	393	374	50δC-NO_2ipb+28δC-OH+18δRing
38		367	362	362	60δRing+24νCN+10 νCO
39		325	326	317	62γC-CH_3+ 23γRing
40		290	276	294	45γNO_2 rock+28δCC+13δRing
41		223	238	225	70 γCH_3 twist+18γRing
42		215	209	209	41γC-NO_2 opb+14γCO+12 γCH_3 twist
43		190	188	191	47γRing+22γC-CH_3+12γCH
44		121	129	120	54γRing+18γC-CH_3+12γCH
45			46	42	35γNO_2twist+23γCH+15CH_3 twist

Table 5: The calculated force constant, IR intensity and Raman activity using DFT method for the HM5NP molecule

Reduced masses	Force constants	IR Intensity	Raman Activity
1.07	9.22	100.95	132.34
1.09	6.58	0.80	68.87
1.09	6.44	9.96	99.26
1.10	6.34	15.48	55.26
1.10	6.28	3.05	61.46
1.04	5.67	8.90	182.93
7.09	11.24	316.75	28.52
7.05	10.77	187.33	36.56
9.73	14.13	132.88	13.03
2.78	3.76	29.27	10.61
1.19	1.55	70.19	3.06
1.07	1.37	19.66	6.43
4.23	5.04	120.82	5.21
1.22	1.45	16.83	11.07
6.61	7.29	362.45	160.43
2.07	2.24	84.82	50.82
5.49	5.71	9.36	28.10
2.18	2.14	198.56	31.62
1.89	1.63	37.19	8.57
1.44	1.19	84.11	21.02
7.99	5.85	54.09	19.56
1.54	1.01	3.08	0.12
1.52	0.96	1.89	6.37
2.86	1.62	10.91	10.25
1.66	0.92	14.28	1.16
10.79	4.67	21.21	11.54
1.50	0.63	24.63	0.28
6.24	2.19	4.48	13.30
7.72	2.65	7.53	0.96
4.68	1.48	1.05	0.32
9.52	2.41	25.93	0.83
4.60	1.00	2.36	4.07
4.53	0.87	2.30	3.06
5.59	0.93	6.98	4.86
2.64	0.33	27.28	0.46
6.50	0.77	5.08	1.84
1.21	0.11	89.48	1.49
7.80	0.60	0.75	2.52
3.46	0.22	0.65	0.36
6.14	0.28	6.55	0.62
7.30	0.24	4.78	0.43
1.36	0.04	1.07	0.95
2.10	0.04	0.06	0.47
6.16	0.03	0.05	0.76
8.96	0.01	0.87	1.08