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Vibrational Spectroscopy

Elixir Vib. Spec. 37 (2011) 3921-3926

ISSN: 2229-712X

Vibrational spectral analysis on 2-hydroxy-4-methyl-3-nitropyridine based on scaled quantum chemical calculation

A.Lakshmi[a], V. Balachandran[b] and A. Janaki[c]
[a]Department of Physics, H.H. The Rajah's College, Pudukkottai 622 001, India
[b]Department of Physics, Arignar Anna Govt. Arts College, Musiri 621 201, India
[c]Department of Physics, Govt. Arts College for Women, Pudukkottai 622 001, India.

ARTICLE INFO
Article history:
Received: 23 May 2011;
Received in revised form:
20 July 2011;
Accepted: 30 July 2011;

Keywords
2-hydroxy-4-methyl-3-nitropyridine,
SQM,
FT-IR and
FT-Raman spectroscopy.

ABSTRACT

The FT-IR and FT-Raman spectra of 2-hydroxy-4-methyl-3-nitropyridine (HMNP) have been recorded and analyzed. The optimized geometry, and harmonic vibrational wave numbers of HMNP have been investigated with the help of B3LYP scaled quantum mechanical (SQM) method supplemented with 6-311++G** basis set. The infrared and Raman spectra were predicted theoretically from the calculated intensities. The observed and simulated spectra were found to be well comparable.

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. In pyridine, pyrazine and in related six member heterocyclic molecules, resonance occurs as in benzene, causing the molecule to be planar and stable. The vibrational spectra of substituted pyridine have been the subject of several investigations [1-3].

Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculations, FT-IR and FT-Raman spectral analyses on 2-hydroxy-4-methyl-3-nitropyridine (HMNP) have no reports. Herein, we reported detailed interpretations of the infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other.

In the present work, we have attempted to interpret the vibrational spectra of HMNP by using B3LYP level of theory throughout with the 6-311++G** basis set implemented in the Gaussian 09 program suite [4].

Methodology

Experimental Details

The fine sample of HMNP was obtained from Lancaster Chemical Company, UK and used as such for the spectral measurements. The FT-Raman spectrum of HMNP was recorded using 1064 nm line of Nd: YAG laser as excitation wave length in the region 3500–100 cm–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 4000–400 cm–1 on Perkin Elmer Spectrophotometer in KBr pellet technique. The observed FT-IR and FT-Raman spectra are shown in Figs.1 and 2, respectively.

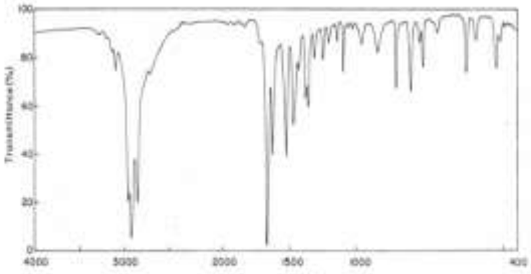

Fig.1 FT-IR spectrum of 2-hydroxy-4-methyl-3-nitropyridine

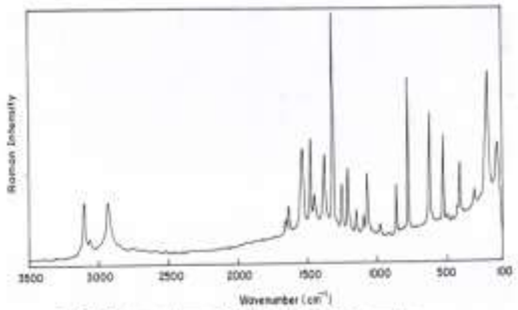

Fig.2 FT-Raman spectrum of 2-hydroxy-4-methyl-3-nitropyridine

Computational methods

Quantum chemical calculations were used for HMNP to carry out the optimized geometry and vibrational wavenumbers with the 2009 version of the Gaussian suite of program using the Becke–3–Lee–Yang–Parr (B3LYP) functional [5,6] supplemented with standard 6-311++G** basis set. The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program [7].The symmetry of the

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Tele:
E-mail addresses: brsbala@rediffmail.com

molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using standard procedure [8] of decomposing the traces of the symmetry operations into irreducible representations. From the basic theory of Raman scattering Raman activities (S_i) calculated by Gaussian 09 program have been converted to relative Raman intensities (I_i) using the following relationship:

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

where γ_o is the exciting wave number (in cm^{-1} units), γ_i is the vibrational wave number of the in *ith* normal mode, *h*, *c*, and *k* are universal constant and *f* is the suitably chosen common scaling factor for all the peak intensities.

The analysis for the vibrational modes of HMNP was presented in some detail in order to better describe the basis for the assignments. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values with wavenumber calculations. The Cartesian representation of the theoretical force constant has been computed at the fully optimized geometry by assuming the molecule belongs to C_s point group symmetry. The transformation force field from Cartesian to internal local symmetry coordinates, scaling the subsequent normal coordinate analysis (NCA), calculation of Potential Energy Distribution (PED) were done on a PC with the version V7.0–G77 of the MOLVIB program written by Sundius [9,10].

A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, a full set of 58 standard internal coordinates containing 13 redundancies were defined as given in Table.1. From these, a non–redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendation of Pulay *et al* [11] and they are presented in Table. 2. The theoretically calculated SQM force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

Result and Discussion

Structure and Symmetry

The optimized structural parameters (Table. 3) and global minimum energy of HMNP were calculated by Cs point group symmetry with B3LYP/6-311++G** level. In accordance with the atom numbering scheme is given in Fig. 3. The global minimum energy of HMNP in Cs point group symmetry is −567.418048 hartrees. The optimized structure of the title compound was compared with other similar systems for which the crystal structures have been solved [12]. From the theoretical values we can find that most of the optimized bond lengths are slightly longer and shorter than experimental values. The computed bond length and bond angles show satisfactory agreement with experimental observation.

Vibrational assignments

The 45 normal modes of HMNP are distributed among the symmetry species as $\Gamma 3N - 6 = 31\ A'$ (in-plane) + $14\ A''$ (out-of-plane) by assuming C_s point group symmetry. The detailed vibrational assignments of fundamental modes of HMNP along with observed and calculated frequencies, IR intensities, Raman scattering activities and normal mode descriptions have been reported in Table 4. It is convenient to discuss the vibrational spectra of HMNP in terms of characteristic spectral region as describe below.

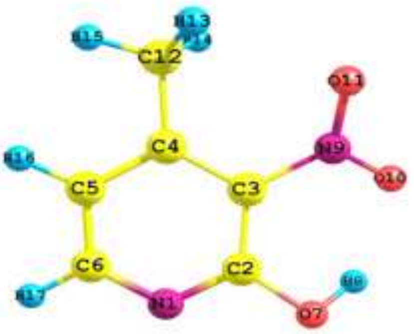

Fig.3 Molecular structure of 2-hydroxy-4-methyl-3-nitropyridine

O–H vibrations

The O–H stretching vibrations normally appear around 3600 cm–1 as in, for phenol [13]. For HMNP, the band values observed at 3510 cm–1 in infrared spectrum and 3495 cm–1 in FT-Raman spectrum are assigned to O–H stretching vibration. The values found at 1426 cm–1 and 749 cm–1 are assigned to O–H in-plane and out-of-plane bending vibrations of HM3NP. These vibrations show good agreement with computed harmonic frequency as well as recorded spectral data.

C–H vibration

The hetero aromatic organic compound 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[14]. In the title molecule, the computed values at 3163, 3140 cm–1 in HMNP 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 [15, 16]. The bands for C–H in-plane bending vibrations of the titled compounds are identified at 1296, 1145 cm–1 in HMNP. The bands observed at 1305, 1150 cm–1 in FT-IR spectrum and 1115 cm–1 in FT-Raman spectrum are assigned to C–H in-plane bending vibrations in HMNP. This assignment is also supported by the literature [15, 16].

CH3 vibration

The title molecule under consideration possesses a CH3 group in the side substituted chain. For the assignments of CH3 group frequencies one can expect that nine fundamentals can be associated to each CH3 group. These vibrations are CH3 ss(symmetric stretching), CH3 ips(in-plane stretching), CH3 ipb (in-plane bending), CH3 sb(symmetric bending), CH3 ipr(in-plane rocking), CH3 opr(out-of-plane rocking), tCH3(twist), CH3ops(out-of-plane), and CH3opb(out-of-plane bending) vibrations. The C–H methyl group stretching vibrations are highly localized and generally observed in the range 3000–2800 cm–1 [17, 18]. In the present investigation, the bands with sharp peaks are found at 3105, 2990, 2970 cm–1 in HMNP are assigned CH3 stretching vibrations. For HMNP, the values observed at 1480, 1460 cm–1 in FT-IR spectrum and 1485 cm–1 in FT-Raman spectrum are assigned to CH3 in-plane and out-of-plane bending vibrations. The values found at 1320 cm–1 and 1032 cm–1 are assigned to CH3 in-plane rock and out-of-plane rock of HMNP molecule. The computed values at 240 cm–1 are assigned to CH3 twisting vibrations of HMNP molecule. This assignment is also supported by the literature.

C□C and C□CH3 vibration

The ring stretching vibrations (C–C) are very much prominent in the spectrum of quinoline and its derivatives are highly characteristic region of the hetero aromatic ring itself [19]. The (C═C) stretching modes are normally observed in the range 1650–1400 cm–1 in benzene derivatives [16]. In the present molecule the values found at 1604, 1600, 1470, 1365, 785 cm–1 in HMNP 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 HMNP molecule. For HMNP, the C–CH3 in-plane vibrations are observed at 505 cm–1 in FT-IR spectrum and 415 cm–1 in FT-Raman spectrum and –CH3 out-of-plane vibrations are observed at 365 cm–1 in FT-Raman spectrum. 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.

The C–C–C bending bands always appear below 600 cm–1 [20]. In the present work, the computed three strong bands present at 610, 585, 380 cm–1 in are assigned C–C–C in-plane bending vibrations. The band identified at 460, 195, 95 cm–1 in HMNP molecule are 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 [21, 22].

C–N and C–NO2 vibrations

The pyridine absorbs strongly in the region 1600–1500 cm–1 due to C═N ring stretching vibrations [23].

Accordingly, a strong bands are identified at 1210, 1075, 1046 cm–1 in HMNP. These bands have strong intensity and some 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 [23-25]. For HMNP molecule the computed C–NO2 in-plane vibration found at 412 cm–1 and it is also observed at 380 cm–1 in FT-Raman spectrum. The values found at 225 cm–1 in HMNP are assigned to C–NO2 out-of-plane vibrations, 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 NO2 group at 1570–1485 and 1370–1320 cm–1, respectively. Hydrogen bonding has little effect on the NO2 asymmetric stretching vibration [26, 27]. The band observed at 1550, 1270 cm–1 in FT-Raman spectrum and 1530, 1270 cm–1 in FT-IR spectrum are assigned to NO2 asymmetric and symmetric stretching vibration of HMNP molecule, respectively. The values found at 857 cm–1 are assigned to scissoring vibrations of HMNP molecule. The other vibrations like 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 [29]. The theoretically computed values are found at 945 cm–1 are assigned to C–O stretching vibration of HMNP. These vibration slightly below the expected range due to the nature and position of the substitution of the methyl and hydroxyl groups. The bands observed at 735, 520 cm–1 in FT-Raman spectrum and 525 cm–1 in FT-IR spectrum are assigned to C–O in-plane and out-of-plane vibrations of HMNP 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.4. 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. They are listed in Table.4.

Conclusion

The IR and Raman frequencies and relative intensities of the vibrational bands of HMNP were calculated at the B3LYP/6-311++G** level of theory. The predicted harmonic frequencies were compared with the experimental data and most of the modes have wave numbers in the expected range. The complete vibrational assignments of wave numbers are made on the basis of potential energy distribution (PED). The excellent agreement of the calculated and observed vibrational spectra reveals the advantages of higher basis set for quantum chemical calculations.

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Table 1 Definition of internal coordinates of HMNP

No.	Symbol	Type	Definition
Stretching			
1-4	Ri	CC aromatic	C2-C3,C3-C4,C4-C5,C5-C6
5	Ri	CC methyl	C4-C12
6-7	Pi	CN aromatic	C2-N1,C6-N1
8	Pi	CN nitro	C3-N9
9-10	Qi	CH aromatic	C5-H16,C6-H17
11-13	Ri	CH methyl	C12-H13,C12-H14,C12-H15
14-15	Pi	NO	N9-O10,N9-O11
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	C4-C5-H16,C6-C5-H16,C5-C6-H17,N1-C6-H17
28-29	βi	CN nitro	C3-N9-O10,C3-N9-O11
30	βi	NO	O10-N9-O11
31-32	βi	bCN	C2-C3-N9,C4-C3-N9
33-34	βi	bCC	C3-C4-C12,C5-C4-C12
35-37	ωi	CCH methyl	C4-C12-H13,C4-C12-H14,C4-C12-H15
38-40	ωi	HCH	H13-C12-H14,H14-C12-H15,H13-C12-H15
41-42	ωi	bCO	N1-C2-O7,C3-C2-O7
43	ωi	bOH	C2-O7-H8
Out-of-plane bending			
44-45	ωi	wCH	H16-C5-C6-C4,H17-C6-N1-C5
46	ωi	CN	C3-N9-O10-O11
47	ωi	CH	C5(C3)-C4-C12-H13(H14,H15)
48	ωi	wCN	N9-C3-C4-C2
49	ωi	wCC	C12-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 HMNP

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 3: Geometrical parameters of HMNP

Bond length	value(Å)		Bond angle	value(Å)	
	Cal.	Expt^a		Cal.	Expt^a
N1-C2	1.33	1.34	C2-N1-C6	118	117
N1-C6	1.33	1.34	N1-C2-C3	122	123
C2-C3	1.43	1.40	N1-C2-O7	115	
C2-O7	1.33		C3-C2-O7	124	118
C3-C4	1.42		C2-C3-C4	120	119
C3(5)-N9(14)	1.45		C2(4)-C3(5)-N9(14)	119	
C4-C5	1.39		C4(6)-C3(5)-N9(14)	121	
C5-C6	1.51	1.40	C3-C4-C5	116	119
C5(3)-H16(9)	1.39	1.08	C3-C4-C12	126	
C6-H17	1.08		C5-C4-C12(10)	118	
O7-H8	1.09		C4-C5-C6	120	118
N9(14)-O10(15)	0.98		C4(2)-C5(3)-H16(9)	120	
N9(14)-O11(16)	1.25		C6(4)-C5(3)-H16(9)	120	
C12(10)-H13(11)	1.22		N1-C6-C5	124	123
C12(10)-H14(12)	1.09		N1-C6-H17	116	
C12(10)-H15(13)	1.09		C5-C6-H17	120	120
			C2-O7-H8	108	
			C3(5)-N9(14)-O10(15)	118	
			C3(5)-N9(14)-O11(15)	120	
			O10(15)-N9(14)-O11(16)	122	
			C4(11)-C12(10)-H13(11)	112	
			C4(11)-C12(10)-H14(12)	112	
			C4-C12-H15	109	
			H13-C12-H14	106	
			H13-C12-H15	109	
			H14-C12-H15	109	109

Taken from Ref.[20]

Table 4: Vibrational assignments of HMNP

S.No.	Observed frequency		Experimental value		Force constants	IR Intensity	Raman Activity	(%PED)/Vibrational assignment
	FT-IR	FT-Raman	Unscaled	Scaled				
1	3510	3495	3417	3410	7.33	256.64	95.45	99νOH
2	3050	3200	3196	3163	6.58	6.58	138.63	85νCH
3	2945		3153	3140	6.39	13.84	134.74	88νCH
4		3110	3125	3105	6.36	17.68	53.55	89νCH$_3$ asym
5		3080	3112	2990	6.27	3.07	61.81	89νCH$_3$ asym
6	2840	2960	3051	2970	5.68	6.73	188.47	89νCH$_3$ sym
7	1605	1630	1625	1604	9.37	205.66	5.20	75νCC+21νOH+12 νNO$_2$
8		1610	1616	1600	9.00	350.79	28.98	65νCC+25νCH+12νCN
9	1550	1530	1580	1565	6.48	60.70	22.27	65νNO$_2$+25 νCN+15δCH
10	1480		1493	1465	2.14	140.71	4.30	82δCH$_3$ ipb+10δCO
11		1470	1482	1470	2.55	49.74	10.15	62νCC+20δCH+10νCN asym
12	1460		1478	1460	1.34	9.12	7.95	88 γCH$_3$ opb
13		1450	1466	1426	3.11	291.83	0.73	72δOH ipb+22CO+13νCC
14		1410	1418	1384	1.44	21.37	10.64	78δCH$_3$ sym+12δOH
15	1390	1385	1398	1365	2.67	52.66	6.40	58νCC+ 20νCC + 12δCH
16		1350	1352	1320	3.13	4.97	43.00	48δCH$_3$ipr+20δOH+15δCH +10δCC
17	1305		1301	1296	2.98	82.25	11.22	75 δCH +20νCC
18	1270	1270	1276	1265	5.56	180.62	84.43	65νNO$_2$+21νCC+ 10νCN
19	1202	1215	1225	1210	2.20	129.55	81.18	42νCN+22δOH+18νCN
20	1150	1115	1164	1145	1.50	9.12	8.30	78δCH+22νCN
21	1080	1045	1084	1075	2.37	33.24	15.18	42νC-NO$_2$+25δCH$_3$ ipb+15δRing
22	1050		1068	1046	2.10	0.21	9.25	42νCN+25νCN+20δCH$_3$ ipr
23	1030		1054	1032	1.01	3.69	0.00	72 γCH$_3$ opr+12 γCH
24		990	998	976	0.83	0.17	0.09	75γCH+12γCH+10γRing
25	995		997	945	1.32	14.10	0.36	48νCO+28δCH$_3$ ipr+18δRing
26	870	875	877	857	4.30	21.26	12.18	65δNO$_2$ sciss+25δRing+12δCH
27		810	833	812	0.49	16.07	0.22	75γCH+12γCH+10γRing
28	785	780	805	785	2.74	2.31	16.65	55νC-CH$_3$+32δRing
29		760	767	749	0.44	55.27	0.48	65γOH+18γCN+10γCH
30		735	739	721	1.89	29.10	0.15	42δCO+21δC-NO$_2$+18γ C-CH$_3$opr
31		650	707	680	1.85	39.04	0.09	55δNO$_2$wagg+30γOH+10γCH
32	610	605	623	610	2.09	14.39	8.66	61δRing+20νCN+12 νCO
33	600	595	590	585	0.73	0.80	0.18	64δRing+20δC-CH$_3$+12δCH
34	525	520	577	565	0.87	1.48	5.20	51γCO+28δC-CH$_3$ ipr+12δCN
35	505	415	541	535	1.27	0.07	11.02	53δC-CH$_3$+22δRing
36	440		477	460	0.52	9.23	0.66	64γRing+20γC-CH$_3$+12γCH
37		380	437	412	0.98	2.96	3.79	50δC-NO$_2$ipb+28δC-OH+18δRing
38		370	395	380	0.52	1.97	1.98	61δRing+20νCN+12 νCO
39		365	370	350	0.36	5.11	1.14	64γC-CH$_3$+ 21γRing
40		310	311	301	0.39	5.74	2.13	45γNO$_2$ rock+28δCC+13δRing
41		260	261	240	0.05	1.33	0.61	72 γCH$_3$ twist+15γRing
42		220	254	225	0.13	0.00	0.47	42γC-NO$_2$ opb+14γCO+12 γCH$_3$ twist
43		205	201	195	0.09	0.41	0.46	45γRing+20γC-CH$_3$+12γCH
44		130	102	95	0.04	0.31	0.54	54γRing+18γC-CH$_3$+12γCH
45			9	8	0.00	1.25	0.47	38γNO$_2$twist+20γCH+15CH$_3$ twist