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Density Functional Theory Calculations on Structures, Vibrational Frequencies of 4-Fluoro-2-Nitroanisole

M.K.Subramanian^{*}, R.Govindarasu and G.Jamuna

Post Graduate and Research Department of Physics, Thiruvalluvar Government Arts College, Rasipuram, Tamilnadu, India.

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ABSTRACT

This work deals with the vibrational spectroscopy of 4-Fluoro-2-Nitroanisole by means of quantum chemical calculations. The FTIR and FT-Raman spectra were measured in the condensed state. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) with the standard B3LYP / $6-311+G^{**}$ basis set combinations, and was scaled using various scale factors which yields a good agreement between observed and calculated frequencies. The vibrational spectra were interpreted with the aid of normal coordinate analysis based on scaled quantum mechanical force field. The results of the calculations were applied to simulated infrared and Raman spectra of the title compound, which showed excellent agreement with the observed spectra.

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Introduction

4-fluoro-2-nitroanisole (4FNA) synthetic are intermediates to other compounds and materials, including plastics, pesticides, pharmaceuticals, and dyes[44]. 4-fluoro-2nitroanisole is used as intermediate for organic synthesis. Due to the interesting properties of 4-fluoro-2-nitroanisole, in the present investigation 4-fluoro-2-nitroanisole was undertaken to study the vibrational spectra of the molecule completely and to identify the various normal modes with greater wavenumbers accurately. Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra. A significant advancement in this area was made by combining semi empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantage. Density functional theory calculations have been performed to support the wave number assignments. The calculated Infrared and Raman spectra of the title compounds were simulated utilizing the scaled force fields and the computed dipole derivatives for IR intensities and polarisability derivatives for Raman intensities.

Experimental Details

The spectroscopically pure sample of 4FNA were obtained and used as such for the spectral measurements. The FT-Raman spectra were recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT-Raman accessories. The spectra were recorded in the region 4000–100 cm⁻¹ with Nd:YAG laser operating at 200mW power continuously with 1064 nm excitation. The room temperature mid Infrared spectra of the title compound were measured in the region 4000–400 cm⁻¹ at a resolution of ± 1 cm⁻¹ using BRUKER IFS 66V vacuum Fourier transform spectrometer equipped with an MCT detector, a KBr beam splitter and globar source.

Computational Details

DFT calculations have been carried out on 4FNA by using GAUSSIAN 09W [20] suite of programs. The calculations employed BECKE's three-parameter exchange function [18], in combination with the correlation with functional of Lee–Yang–Parr (LYP) [19]. All of the calculations were performed with the B3LYP/6-311+G** basis sets.

All the geometrical parameters of 4FNA were fully optimized. The vibrational frequencies, IR intensities and Raman activities were also obtained. In order to obtain a more complete description of the molecular motions, normal mode analysis has been carried out. The harmonic force fields in Cartesian coordinates that resulted from DFT procedure were converted to the force fields in the desired internal coordinates. These force fields were subsequently used to reproduce the DFT vibrational frequencies and determine the TED by means of Wilson's GF matrix method, which made it possible to obtain a detailed description of the nature of vibrational bands. In order to improve the agreement between the computational and observed frequencies, the scaling method suggested by Pulay [28] was used with a scale factor. The Raman activities (Si) calculated by the GAUSSIAN 09W

The Raman activities (Si) calculated by the GAUSSIAN 09W program were converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering[2],

$$I_{i} = \frac{f(v_{o} - v_{i})^{4} S_{i}}{v_{i} [1 - \exp(-hcv_{i} / KT)]}$$

Where υ_0 is the exciting frequency (in cm⁻¹), υ_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

Tele: E-mail address: profdrmks@gmail.com

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Results and Discussion

Molecular geometry

The optimized molecular structure of 4FNA belongs to C_s point group symmetry and is shown in Fig. 4.1. The global minimum energy obtained by the DFT structure optimization for the title compound is presented in Table 4.1. The bond lengths and bond angles determined at the DFT level of theory for the 3BNA compound are listed in Table 4.2.

Table 4.1. Total energies of 4FNA, calculated at DFT
(B3LYP)/6-31G* and (B3LYP)/6-311+G** level.

Method	Energies (Hartrees)
6-31G*	-1463.362642
6-311+G**	-1463.539867



Fig 4.1. The optimized molecular structure of 4FNA. Vibrational spectra

According to the theoretical calculations, 4FNA has a planar structure of C_s point group symmetry. The 48 normal modes of vibrations are distributed among the symmetry species as $\Gamma_{3N-6}=33$ A'(in plane)+15 A" (out of plane).

Detailed description of vibrational mode can be given by means of normal coordinate analysis (NCA). For this purpose, the set of 62 standard internal coordinates containing 14 redundancies are defined as given in Table 4.3. From these a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi et al. [27] are summarized in Table 4.4.

Table 4.3. Definition of internal coordinates of 4FNA.							
No(i)	symbol	Туре	Definition				
Streching	Ri	C-C(ring)	C1-C2,C2-C3,C3-C4,C4-				
1-6		(<i>U</i>)	C5.C5-C6.C6-C1				
7-9	r:	C-H(aro)	С3-Н18 С4-Н17 С6-Н16				
10-11	S:	C-O(sub)	C2-08 C10-08				
12	S ₁	C-N(sub)	C1-N7				
12	s _i	C = F(sub)	C5 E0				
13	Pi D	C-F(Sub)	C10 U12 C10 U14 C10				
14-10	ri	C-H(methyl)	С10-П13,С10-П14,С10-				
17.10		NO(1)					
1/-18	n _i	N-O(sub)	N/-011,N/-012				
Bending	ρ_i	C-C-C(ring)	C1-C2-C3,C2-C3-C4,C3-				
19-24			C4-C5,				
			C4-C5-C6,C5-C6-C1,C6-				
			CI-C2				
			С2-С3-Н18,С4-С3-Н18,				
25-30	θ_i	С-С-Н	С3-С4-Н17,С5-С4-Н17,				
			C5-C6-H16,C1-C6-H16.				
31-33	βi	C-C-O	C1-C2-O8,C3-C2-O8,C2-				
			O8-C10				
34-35	Φ_{i}	C-C-N	C6-C1-N7, C2-C1-N7				
36-37	Ψi	C-C-F	C4-C5-F9, C6-C5-F9				
38-40	αί	Н-С-Н	H13-C10-H14, H14-C10-				
		(methyl)	H15,				
			H15-C10-H13				
41-43	Vi	O-C-H	O8-C10-H13, O8-C10-H14,				
	1.	(methyl)	O8-C10-H15				
44-45	11:	C-N-O	C1-N7-011 C1-N7-012				
46	μ_1	0-N-0	012-N7-011				
Out-of-	V1 (0)	0.0	08-C2-C1-C3				
nlane	ψ_1	0-0	00-02-01-03				
17							
47	۶.	NO	C1 N7 O11 O12				
40 51	Si	N-0	H18 C2 C2 C4 H17 C4				
49-51		СЧ	C2 C5				
	ωi	С-п	U_{3} - U_{3} , U_{16} C6 C5 C1				
50	1	CN	N7 C1 C2 CC				
52	Λ _i	C-N	N/-CI-C2-C6				
53	σi	C-F	F9-C5-C4-C6				
Torison	$ au_{i}$	τC-O	C1(C3)-C2-O8-C10				
54		(methyl)					
			C1-C2-C3-C4,C2-C3-C4-				
55-60	$ au_i$	τring	C5,				
			C3-C4-C5-C6,C4-C5-C6-				
			C1,				
			C5-C6-C1-C2,C6-C1-C2-				
			C3				
61	τι	τО-С-Н	C2-O8-C10-(H13,H14,H15)				
		(methyl)					
62	τι	τN-O	C2(C6)-C1-N7-O11(O12)				

The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

ahle	4 2	Ontimized	l geometrical	narameters of	4FNA	obtained by	B3LVP/	6_311+C**	density	v functional	calculatio	ne
able	4.2.	Optimizet	i geometi itai	par ameters or	HIINA	obtained by		0-311+G	uensity	Tuncuonai	calculatio	112

inzed geometrical parameters of 41 the obtained by B3L117 0-311+G density function										
Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)					
C2-C1	1.3860769	C3-C2-C1	119.9981649	C4-C3-C2-C1	0.0000000					
C3-C2	1.3860000	C4-C3-C2	119.9981649	C5-C4-C3-C2	0.0000000					
C4-C3	1.3860769	C5-C4-C3	120.0016034	C6-C5-C4-C3	0.0000000					
C5-C4	1.3859903	C6-C5-C4	120.0016034	N7-C1-C2-C3	179.4280997					
C6-C5	1.3859903	N7-C1-C2	119.9989958	O8-C2-C1-C6	-179.4275424					
N7-C1	1.4460540	O8-C2-C1	119.9986499	F9-C5-C4-C3	179.4272131					
O8-C2	1.4099698	F9-C5-C4	119.9970317	C10-O8-C2-C1	120.0024185					
F9-C5	1.4899884	C10-O8-C2	109.4985657	O11-N7-C1-C2	0.5719142					
C10-C8	1.4100826	011-N7-C1	120.0004740	O12-N7-C1-C2	-178.8537249					
O11-C7	1.1317415	O12- N7-C1	119.9981135	H13-C10-O8-C2	180.0000000					
O12-C7	1.3160201	H13-C10-O8	109.4981558	H14-C10-O8-C2	59.9293864					
H13-C10	1.1219722	H14- C10-O8	109.4984345	H15-C10-O8-C2	-59.9324109					
H14-C10	1.1219194	H15- C10-O8	109.4965441	H16-C6-C5-C4	-179.4280298					
H15-C10	1.1219732	H16-C6-C5	119.9964765	H17-C4-C3-C2	179.4280627					
H16-C6	1.1219722	H17-C4-C3	119.9969288	H18-C3-C2-C1	179.4280047					
H17-C4	1.1220419	H18-C3-C2	120.0008192							
H18-C3	1.1219722									

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No.(i)	No.(i) Symbol ^a Definition ^b		Scale factors used in calculation
1-6	C-C	R1,R2,R3,R4,R5,R6	0.914
7-9	C-H(aro)	r7,r8,r9	0.914
10-11	C-O(sub)	S10,S11	0.992
12	C-N(sub)	s12	0.992
13	C-F(sub)	p13	0.995
14	CH3ss	(P14+P15+P16)/ \sqrt{3}	0.992
15	CH3ips	(2P15-P14-P16)/ √6	0.919
16	CH3ops	(P15-P16)/ \sqrt{2}	0.992
17	NOss	(n17+n18)/ \sqrt{2}	0.992
18	NOas	(n17-n18)/ √2	0.992
19	C-C-C(ring)	(p19-p20+p21-p22+p23-p24)/ √6	0.916
20	C-C-C(ring)	(2p19-p20-p21+2p22-p23-p24)/√12	0.923
21	C-C-C(ring)	(p20-p21+p23-p24)/2	0.923
22-24	C-C-H	$(\theta 25 - \theta 26)/\sqrt{2}, (\theta 27 - \theta 28)/\sqrt{2},$	0.990
		$(\theta 29 - \theta 30)/\sqrt{2}$	
25-26	C-C-O	(β31-β32)/√2, β33	0.990
27	C-C-N	(Ф34-Ф35)/√2	0.990
28	C-C-F	(ψ36-ψ37)/√2	0.990
29	CH3sb	(α38+α39+α40-γ41-γ42-γ43)/ √6	0.990
30	CH3ipb	(2α40-α38-α39)/ √6	0.994
31	CH3opb	$(\alpha 38 - \alpha 40) / \sqrt{2}$	0.962
32	CH3ipr	(2γ42-γ41-γ43)/ √6	0.962
33	CH3opr	(γ41-γ43)/ √2	0.994
34	NO2sc	(2v44-µ45-µ46)/√6	0.994
35	NO2r	(µ45-µ46)/ √2	0.994
36	O-C	φ47	0.979
37	N-O	ξ48	0.914
38-40	C-H	ω49, ω50, ω51	0.914
41	C-N	λ52	0.992
42	C-F	σ53	0.992
43	C-O(methyl)	τ54	0.995
44	tring	$(\tau 55 - \tau 56 + \tau 57 - \tau 58 + \tau 59 - \tau 60)/\sqrt{6}$	0.992
45	tring	(τ55-τ57+τ58-τ60)/2	0.919
46	tring	$(-\tau 55+2\tau 56-\tau 57-\tau 58+2\tau 59-\tau 60)/\sqrt{12}$	0.992
47	O-C-H(methyl)	τ61/3	0.992
48	N-O	τ62/4	0.992

 Table 4.4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for 4FNA.

For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of the title compound are presented in Fig. 4.2 and Fig. 4.3, respectively. Comparison between calculated and observed vibrational spectra helps us to understand the observed spectral features.



Fig 4.2. FT-IR spectra of 4FNA (a) Observed (b) Calculated with B3LYP/6-311+G**.



Fig 4.3. FT-Raman spectra of 4FNA (a) Observed (b) Calculated with B3LYP/6-311+G**

The detailed vibration assignments of the observed and calculated vibrational wavenumbers, theoretical Infrared intensities, Raman scattering activities and Raman intensities are listed in Table 4.5.

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Table 4.5. Detailed assignments of fundamental vibrations of 4FNA by normal mode analysis based on SQM force field calculation

	Symmetry species	Observed f	frequency	Calculated frequency (cm ⁻¹) with			vith	TED (%) among type of internal coordinates ^c
	9	(cm ⁻¹)		B3LYP/6-311+G ^{**} force field				
S. No.	C_s	Infrared	Raman	Unscaled	Scaled	IR ^a	Raman ^b	
						A _i	I _i	
1	Α'	3290		3295	3289	26.824	69.285	CH(99)
2	Α'	3264		3270	3264	5.143	50.248	CH(99)
3	Α'	3240	3240	3245	3238	1.087	130.192	CH(99)
4	Α'	3220		3228	3221	2.699	63.966	CH(99)
5	Α'	3165	3164	3171	3164	16.837	83.001	CH3ops(98)
6	Α'	3075	3078	3086	3078	52.934	98.412	CH3ss(96)
7	Α'		1686	1693	1685	135.380	15.267	CC(39),NOas(32),bCH(8),bring(6),bNO2r(6),bCCN(5)
8	Α'	1654		1660	1653	128.509	30.846	NOas(43),CC(38),bCH(8),bring(5)
9	Α'	1632		1637	1631	26.392	22.204	CC(69),bring(9),NOas(8),bCH(7)
10	Α'		1555	1562	1554	11.449	15.130	bCH3ip(72),bCH3op(26)
11	Α'			1660	1547	118.360	3.930	bCH(33),CC(31),bCH3sb(17),CO(11)
12	A'	1530	1531	1539	1532	2.964	21.996	bCH3op(75),bCH3ip(23)
13	A'	1502		1506	1500	36.998	6.090	bCH3sb(70),bCH(14),CC(10)
14	A'	1456	1458	1465	1457	5.547	1.187	CC(54),bCH(28)
15	A'	1412		1421	1413	247.745	85.576	NOss(67),bNO2sc(15),CN(14)
16	A'	1353	1355	1358	1353	1.502	5.409	CC(88)
17	A'			1313	1310	150.222	30.989	CO(42),CC(21),bCH(17),bCH3sb(5),bring(5)
18	A'	1287	1289	1292	1286	18.655	6.705	bCH(58),CC(19),CO(9)
19	A'			1229	1222	2.167	5.331	bCH3op(41),bCH3ip(40),bCH3ip(8)
20	A"	1187		1196	1189	13.141	16.924	bCH(56),CC(28),CN(6)
21	A'		1184	1191	1185	1.441	9.061	bCH3ip(39),bCH3op(37),bCH3op(13),bCH3ip(8)
22	A'	1132		1142	1135	75.591	16.080	CC(35),bring(21),bCH(16),CCl(16),CN(6)
23	A'			1120	1114	25.462	3.278	CC(29),bCH(25),bring(16),CN(15),CO(8)
24	A'		1052	1057	1050	68.730	8.158	CO(72),bring(16),CC(5)
25	A"			984	976	0.128	0.571	gCH(86),tring(12)
26	A"		923	926	922	10.984	1.865	gCH(70),tring(19),gCN(5)
27	A'	900		908	901	25.153	1.846	bring(30),bNO2sc(26),CN(14),CF(12),NOss(7)
28	A"			868	863	24.835	3.198	gCH(65),tring(12),gOC(11)
29	A'	824	820	827	821	17.961	20.480	bNO2sc(26),bring(20),CC(17),CO(17),gCH(7)
30	A"			792	787	4.943	0.375	gCNO(36),gCN(24),tring(20),gOC(9),gCH(6)
31	A"			748	741	38.698	0.870	tring(30),gOC(12),bring(8),bNO2sc(7),gCNO(6),CF(5)
32	A"	690		698	691	6.092	3.178	tring(41),bring(15),gOC(10),gCF(8)
33	A'	654	652	658	653	18.875	3.018	bring(38),tring(21),CF(17),gCF(6),CO(5)
34	A'	601		604	599	5.031	1.028	bNO2r(24),bCCO(15),gCN(11),tring(10),CC(9),bCCN(8)
35	A"			579	574	14.279	0.625	tring(41),gCF(30),gOC(11),gCH(5),bCCO(5)
36	A"			468	463	4.862	0.718	tring(30),bCCO(24),gCN(22)
37	A"			432	423	1.515	0.968	tring(61),gCH(12),gCF(8),bCCO(7)
38	A'		İ	391	385	0.431	2.725	bring(29),bCF(23),CN(18),bNO2r(7)
39	A'		381	385	381	1.193	3.570	bNO2r(26),tring(19),bCCO(16),CF(10),gCN(8),CC(5)
40	Α'			362	354	1.392	4.345	bring(35),tring(16),CF(11),gCF(9),gCN(6)

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41	A'		289	283	1.892	1.510	bCF(35),bCCO(19),bCCN(12),tCOm(11),CC(8),tOCH3(6)
42	A'	224	236	229	3.474	2.982	bCCO(34),gOC(24),tring(20),gCF(7)
43	A"	180	183	178	2.051	0.944	bCCN(55),bCF(26),CC(5)
44	A"		167	159	1.557	2.080	gCN(43),tring(17),gCH(13),gCF(10),gCNO(5)
45	Α'		161	156	0.195	0.429	tOCH3(80),bCCO(8)
46	A"		125	119	4.215	0.817	tCOm(70),gCN(8)
47	A"		121	121	1.232	2.053	tring(47),tCOm(23),bCCO(8),gCH(7),gOC(5)
48	A"		117	117	0.277	1.393	tNO(40),tCOm(32),bCCO(13)

In the last column is given a detailed description of the normal modes based on the TED. It is seen that the overall agreement between the calculated wavenumbers and the experimental values is very good. This confirms the reliability of the presented band assignments.

Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$RMS = \sqrt{\frac{1}{n-1} \sum_{i}^{n} \left(\upsilon_{i}^{calc} - \upsilon_{i}^{exp}\right)^{2}}$$

The RMS error of frequencies $(B3LYP/6-311+G^{**})$ obtained for 4FNA was found to be 109 cm⁻¹. In order to reproduce the observed frequencies, refinement of scaling factors was applied and optimized via least square refinement algorithm which resulted a RMS deviation of 9.35 cm⁻¹. The good agreement allows us to perform the assignments of the IR and Raman bands to the normal modes in the whole studied spectral regions.

C-H vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region $3100-3000 \text{ cm}^{-1}$ due to aromatic C–H stretching vibrations. Accordingly, in the present study the C– H vibrations of the title compounds are observed at 3290,3264, 3240 and 3220 cm⁻¹ in the FTIR spectrum and 3240 cm⁻¹ in Raman for 4FNA. The bands due to C–H inplane ring bending vibration interacting somewhat with C–C stretching vibration are observed as a number of sharp bands in the region 1300–1000 cm⁻¹. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 970–667 cm⁻¹.

The in-plane and out-of-plane bending vibrations of C–H have also been identified at 1286, 1222, 1189 cm⁻¹ and 976,922,863 cm⁻¹ for the title compound.

C–O vibrations

If a compound contains a carbonyl group, the absorption caused by the C–O stretching is generally strongest. Considerations of these factors lead to assign the band observed at $1310,1286, 1050, 863 \text{cm}^{-1}$ to C–O stretching vibrations for the title compound.

C-C vibrations

The C-C aromatic stretching predicted at 1631, 1457, 1353 cm⁻¹ and 1458,1355 cm⁻¹ is in excellent agreement with experimental observations of both in FTIR and FT-Raman spectra. These observed frequencies show that, the substitutions in the ring to some extent about the ring mode of vibrations. [36]. The theoretically calculated C-C out-of-plane and in-plane bending modes have been found to be consistant with the recorded spectral values.

Ring vibrations

Several ring modes are affected by the substitution to the aromatic ring of 4FNA. In the present study, the bands ascribed at 1135, 1050, 976, 922 cm⁻¹ and 863, 787, 741 cm⁻¹ [45]for 4FNA have been designated to ring in-plane and out-of-plane bending modes, respectively, by careful consideration of their quantitative descriptions. A small change in frequency observed for these modes are due to the changes in force constant/reduced mass ratio.

C-F vibrations

The C-F stretching gives generally strong bands in the 900–505 cm⁻¹ region. The sharp FT-IR and FT-Raman bands at 901, 741, 691, 653, 574 cm⁻¹ respectively observed in the spectrum of the title compound are assigned to C-F stretching vibration.

Nitro vibrations

Aromatic nitro compounds have strong absorptions due to asymmetric and symmetric stretching vibrations of the nitro group. Usually, the symmetric vibration is stronger than antisymmetric one in the Raman spectra and the contrary holds in infrared. This could be due to the electron withdrawing substituent adjacent to the nitro group tend to increase the frequency of asymmetric vibration and decrease that of the symmetric vibration. The symmetric stretching vibrations of this group were found intense at 1654 cm⁻¹ in FT-IR and 1686 cm⁻¹ in FT-Raman. The ring stretching vibrations are interesting, as the double bond is in conjugation with the ring and are well found in the characteristic regions. **Methyl group vibrations**

The 4FNA compound, under consideration possesses only one CH₃ group in the ring, respectively. For the assignments of CH₃ group frequencies, one can expect that nine fundamentals can be associated to each CH₃ group, namely the symmetrical (CH₃ ips) and asymmetrical (CH₃ ops), inplane stretching modes (i.e. in-plane hydrogen stretching mode); the symmetrical (CH₃ ss), and asymmetrical (CH₃ ips), deformation modes; the in-plane rocking (CH₃ ipr) out-of-plane rocking (CH₃ opr) and twisting (t CH₃) bending modes. In addition to that, the asymmetric stretching (CH₃ ops) and asymmetric deformation (CH₃ opb) modes of the CH₃ group are expected to be depolarised for A" symmetry species. In the present work, the frequencies observed in the infrared band found at 3165 cm⁻¹ and 3078 cm⁻¹ represent symmetric and asymmetric CH₃ stretching vibrations of the methyl group in 4FNA which are found to be well within their characteristic region.

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