

Density Functional Study on the Vibrational Frequencies of Hydrazoic Acid and Methyl Azide

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Abstract: Harmonic vibrational frequencies of hydrazoic acid and methyl azide are calculated using HF, MP2 methods and five popular density functional (DFT) methods and compared with experimental results. Of these seven methods, BLYP reproduces the observed frequencies most satisfactorily, while the results in HF and MP2 are worse. These indicate the BLYP calculation is a very promising approach for understanding the observed spectral features.

Keywords: Density functional theory; vibrational spectra, hydrazoic acid, methyl azide.

Density functional theory (DFT)^{1,2} is gaining popularity recently as a cost-effective general procedure for studying physical properties of molecules. Unlike the Hartree-Fock theory, DFT recovers electron correlation in the self-consistent Kohan-Sham procedure through the functionals of electron density and gives good descriptions for systems which require sophisticated treatments of electron correlation in the conventional *ab initio* approach³. Although DFT was not favored by computational chemists for many years, it was recently paid much attention by many *ab initio* quantum chemists and much effort has been devoted to refining the methodology and exploring its applicability⁴⁻⁵. DFT calculations of vibrational spectra of small organic systems⁴⁻⁵ have shown promising conformity with experimental results. In a recent comprehensive study, Raulhut and Pulay⁶ have shown that the raw BLYP and B3LYP frequencies and force constants approximate the experimental results much better than the Hartree-Fock results, and the use of multiple scale factors further improves the agreement between the calculated and observed fundamental vibrational frequencies.

The infrared spectra of gaseous methyl azide (CH₃N₃), deuterio-methyl azide (CD₃N₃), hydrazoic acid (HN₃) and deuterio-hydrazoic acid (DN₃) have been published⁷⁻¹¹. Although some earlier force-constant calculations have been reported, there has been no DFT calculation of vibrational frequencies for these compounds. In this paper, we calculate the harmonic frequencies of hydrazoic acid and methyl azide using five different DFT, HF and MP2 methods and compare these results with experimental vibrational frequencies. Furthermore, the effect of deuterio-substitution is also calculated and discussed. Some beneficial results have been given.

All calculations were carried out using the Gaussian 94 program package. Five popular DFT methods are used in this study. They are: BLYP, BP86, LSDA, B3LYP and B3P86. The 6-31G* basis set was used throughout. This basis set was chosen on the basis of the findings that the 6-31G* DFT results on structures, energies, and force constants are obviously superior to results of smaller basis sets. However, further enlarging the basis set increases the computational cost significantly and therefore is not practical for studying larger systems. All molecular structures were fully optimized prior to analytic second derivative calculations and vibrational analysis.

Table 1 Calculated and experimental fundamental vibrational frequencies (cm^{-1}) of HN_3

Sym.	Exp.	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	3336	3347	3445	3375	3470	3509	3722	3518	NH str.
A'	2140	2184	2322	2217	2294	2329	2509	2390	NN str.
A'	1274	1261	1332	1272	1313	1329	1452	1267	NNNH bend.
A'	1150	1151	1124	1156	1196	1201	1254	1129	NNN str.
A''	637	572	606	579	603	611	677	575	NNN opb.
A'	522	507	541	514	529	537	572	550	NNN ipb.
Mean deviation		-6.2	35.2	9.0	57.7	77.8	187.8	64.2	
Mean abs. Dev.		24.8	54.2	31.7	69.0	86.5	187.8	94.2	
Standard dev.		36.5	87.8	46.7	96.5	121.1	257.6	142.7	

Table 2 Calculated and experimental fundamental vibrational frequencies (cm^{-1}) of DN_3

Sym.	Exp.	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	2480	2449	2525	2470	2539	2568	2721	2579	ND str.
A'	2141	2175	2312	2209	2287	2322	2505	2375	NN str.
A'	1183	1203	1311	1231	1260	1290	1273	1229	NNND bend.
A'	955	933	892	925	966	959	1104	916	NNN str.
A''	638	557	595	566	591	599	620	562	NNN opb.
A'	498	478	505	484	498	504	539	508	NNN ipb.
Mean deviation		-16.7	40.8	-1.7	41.0	57.8	152.8	45.7	
Mean abs. Dev.		34.7	76.2	40.3	56.7	70.8	152.8	84.0	
Standard dev.		44.6	103.5	51.6	81.3	103.5	211.5	121.7	

Results and discussion

Hydrazoic acid is a planar molecule belonging to the C_s point group. There are five frequencies belonging to species A' and one frequency belongs to the species A'' . Similarly, methyl azide also belongs to C_s point group. Ten symmetry coordinates belong to species A' and five symmetry coordinates belong to species A'' . The calculated frequencies and the experimental frequencies⁷⁻¹¹ are given in **Table 1-4** for HN_3 , DN_3 , CH_3N_3 and CD_3N_3 . The mean deviation, mean absolute deviation and standard deviation between the calculated harmonic and the experimental vibrational frequencies for each method are also given in **Table 1-4**. Overall mean deviation, mean absolute deviation and standard deviation are given in **Table 5**.

Results in **Table 1-4** indicate that frequencies calculated by all two hydride DFT methods are higher than experimental frequencies. Overall mean absolute and standard deviations between the experimental frequencies and calculated frequencies are 56.1 and 80.6 cm^{-1} for B3LYP, 69.4 and 100.0 cm^{-1} for B3P86. The other three DFT methods, BLYP, LSDA and BP86 yield a much higher level of conformity between the calculated

Table 3 Calculated and experimental fundamental vibrational frequencies (cm^{-1}) of CH_3N_3

Sym.	Exp.	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	3023m	3089	3096	3113	3174	3192	3329	3248	Asym. CH_3 str.
A''	2962m	3012	3020	3034	3098	3117	3258	3186	Sym. CH_3 str.
A'	2935m	2957	2958	2968	3038	3050	3200	3101	Asym. CH_3 str.
A'	2106vs	2149	2186	2299	2264	2300	2474	2375	Asym. NNN str.
A''	1538m	1483	1474	1458	1523	1519	1643	1553	CH_3 wag.
A'	1447s	1482	1473	1455	1521	1517	1641	1557	Asym. CH_3 def.
A'	1417s	1432	1424	1422	1474	1472	1602	1498	Sym. CH_3 def.
A'	1272vs	1285	1313	1394	1349	1380	1388	1335	sym NNN str.
A'	1132m	1132	1123	1119	1115	1159	1269	1175	CH_3 rock
A''	1036vs	1085	1080	1078	1120	1119	1223	1147	CH_3 rock
A'	910s	873	897	962	926	949	1015	934	CN str.
A'	666s	635	641	655	665	671	737	686	CNNN bend
A''	560m	535	542	569	574	581	669	552	NNN bend
A'	245	239	239	238	247	247	275	232	CNNN bend
A''	126	107	107	95	103	103	115	148	CH_3 torsion
Mean deviation		8.1	12.9	36.1	50.6	66.5	164.2	90.1	
Mean abs. Dev.		32.3	34.0	51.5	57.9	72.1	165.7	92.9	
Standard Dev.		38.5	42.9	75.1	81.7	97.7	201.2	130.5	

w, m, s, v =weak, medium, strong, very.

Table 4 Calculated and experimental fundamental vibrational frequencies (cm^{-1}) of CD_3N_3

Sym.	Exp.	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	3023m	3089	3096	3113	3174	3192	3329	3248	Asym. CH_3 str.
A''	2962m	3012	3020	3034	3098	3117	3258	3186	Sym. CH_3 str.
A'	2935m	2957	2958	2968	3038	3050	3200	3101	Asym. CH_3 str.
A'	2106vs	2149	2186	2299	2264	2300	2474	2375	Asym. NNN str.
A''	1538m	1483	1474	1458	1523	1519	1643	1553	CH_3 wag.
A'	1447s	1482	1473	1455	1521	1517	1641	1557	Asym. CH_3 def.
A'	1417s	1432	1424	1422	1474	1472	1602	1498	Sym. CH_3 def.
A'	1272vs	1285	1313	1394	1349	1380	1388	1335	sym NNN str.
A'	1132m	1132	1123	1119	1115	1159	1269	1175	CH_3 rock
A''	1036vs	1085	1080	1078	1120	1119	1223	1147	CH_3 rock
A'	910s	873	897	962	926	949	1015	934	CN str.
A'	666s	635	641	655	665	671	737	686	CNNN bend
A''	560m	535	542	569	574	581	669	552	NNN bend
A'	245	239	239	238	247	247	275	232	CNNN bend
A''	126	107	107	95	103	103	115	148	CH_3 torsion
Mean deviation		8.1	12.9	36.1	50.6	66.5	164.2	90.1	
Mean abs. Dev.		32.3	34.0	51.5	57.9	72.1	165.7	92.9	
Standard Dev.		38.5	42.9	75.1	81.7	97.7	201.2	130.5	

w, m, s, v =weak, medium, strong, very.

Table 5 Overall mean deviations, mean absolute deviations, and standard deviations (cm^{-1})

	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2
Mean deviation	-6.3	28.3	10.7	46.2	61.0	156.7	64.9
Mean abs. Dev.	29.1	51.6	38.0	56.1	69.4	161.1	90.5
Standard dev.	38.8	74.7	53.1	80.6	100.0	212.2	131.7

results and the experimental vibrational frequencies. The overall mean absolute and standard deviations are 29.1 and 38.8 cm^{-1} for the BLYP results, 51.5 and 74.7 cm^{-1} for the LSDA results, 14.2 and 53.1 cm^{-1} for BP86 results. Compared to the experimental

frequencies of these three DFT methods, LSDA gives the largest deviations, whereas BLYP and BP86 perform very similarly with deviations of BLYP results being slightly smaller.

The calculated harmonic frequencies of HF and MP2 methods at 6-31G* basis set are also listed in **Table 1-4**. As we can see, even at MP2 level, the larger deviations are found compared with five DFT methods. The worst agreement between the calculated and observed results is found with HF/6-31G* results, even when the scale factors were considered, the results are still worse than DFT methods.

We investigated the changes in the infrared spectral features for the isotopomer relative to the neutral nondeuterated HN_3 and CH_3N_3 . The largest effects in HN_3 molecule appear on the NH stretch, which has decreased by about 850 cm^{-1} due to the deuterio-substitution. Similarly, NNNH bending band only decreased by 90 cm^{-1} . The NN stretch and NNN outer place bending remain effectively unchanged in frequency. In the CH_3N_3 molecule, The mainly effects in frequency appear on the symmetric CH_3 stretch, asymmetric CH_3 stretch, CH_3 rock and CH_3 torsion. The NNN bend and NNN stretch remains effectively unchanged in frequency.

Conclusions

Comparison of the calculated and experimental results indicates that the BLYP reproduces the observed fundamental vibrational frequencies satisfactorily with mean absolute deviations of less than 29.1 cm^{-1} and standard deviations of about 38.8 cm^{-1} . Therefore, it is a promising approach for identifying observed spectral features due to the fundamental modes and for identifying an unknown compound by comparing its vibrational spectrum with calculated results of a few candidates.

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