

## Vibrational frequencies of hydrazoic acid and methyl azide: density functional theory study

ZHOU, Zheng-Yu<sup>\*,a,b</sup>(周正宇)    DU, Dong-Mei<sup>a</sup>(杜冬梅)    FU, Ai-Ping<sup>a</sup>(付爱萍)  
YU, Qing-Sen<sup>c</sup>(俞庆森)

<sup>a</sup> Department of Chemistry, Qufu Normal University, Qufu, Shandong 273165, China

<sup>b</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong 250100, China

<sup>c</sup> School of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, China

Harmonic vibrational frequencies of  $\text{HN}_3$  and  $\text{CH}_3\text{N}_3$  molecules and their several isotopomers are calculated using HF, MP2 and five popular density functional theory (DFT) methods. On the basis of the comparison between calculated and experimental results, assignments of fundamental vibrational modes are examined. HF and MP2 results are in bad agreement with experimental values. Of the five DFT methods, BLYP reproduces the observed fundamental frequencies the most satisfactorily. Two hybrid DFT methods are found to yield frequencies generally higher than the observed fundamental frequencies. The results indicate that BLYP calculation is a very promising approach for understanding the observed spectral features.

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

### Introduction

Density functional theory (DFT)<sup>1-4</sup> is gaining popularity recently as a cost-effective general procedure for studying chemical reactions and physical properties of molecules. Unlike the Hartree-Fock theory, DFT recovers electron correlation in the self-consistent Kohn-Sham procedure through the functions of electron density and gives good descriptions for systems, which require sophisticated treatments of electron correlation in the conventional *ab initio* approach. 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 applicability. DFT calculations of vibrational spectra of small organic systems<sup>5-8</sup> have shown promising conformity with experimental results. In a recent comprehensive study, Raulhut and Pulay<sup>9</sup> 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 methyl azide ( $\text{CH}_3\text{N}_3$ ), deuterio-methyl azide ( $\text{CD}_3\text{N}_3$ ), hydrazoic acid ( $\text{HN}_3$ ) and deuterio-hydrazoic acid ( $\text{DN}_3$ ) have been published.<sup>10-14</sup> Recently, *ab initio* calculations of vibrational frequencies and geometries for these compounds have been carried out at HF/6-31G<sup>\*\*</sup> and MP2/6-31G<sup>\*\*</sup> level.<sup>15</sup> The results indicate that the HF and MP2 calculated frequencies are not in good agreement with experimental spectra. To gain a better understanding of the performance and limits of different DFT methods as a general approach to the vibration problems of many molecules, we calculated harmonic frequencies of hydrazoic acid, methethyl azide by five different DFT, HF and MP2 methods and compared these results with experimental vibrational frequencies. Furthermore, the effect of deuterio-substitution is also discussed. Some beneficial results have been given.

Received August 23, 1999; accepted December 3, 1999.

Project supported by the Natural Science Foundation of Shandong Province, the National Key Laboratory Foundation of Crystal Material and the National Natural Science Foundation of China (No. 2967305).

## Calculation

All calculations were carried out using the Gaussian 94 program package. Five popular DFT methods were used in this study. They are: Slater's (local spin density) exchange functional<sup>16</sup> in conjunction with Vosko-Wilk-Nusair correlation functional<sup>17</sup> (LSDA), Becke's gradient-corrected exchange functional<sup>18,19</sup> in conjunction with Lee-Yang-Parr gradient-corrected exchange functional<sup>20</sup> (BLYP), Becke's gradient-corrected exchange functional in conjunction with Perdew gradient corrected correlation functional<sup>21</sup> (BP86), Becke's three-parameter method<sup>22</sup> with Perdew correlation functional (B3P86) and Becke's three-parameter method with Lee-Yang-Parr correlation functional (B3LYP). 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.<sup>23</sup> Further enlarging the basis set, however, 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.

## Results and discussion

### Structures

The equilibrium structural parameters of hydrazoic acid and methyl azide are calculated by different methods and compared with available experimental data.<sup>24,25</sup> The results indicate that all the calculated structural parameters are in agreement with available experimental results. The HF/6-31G\* bond lengths are slightly shorter, while the BLYP/6-31G\* bond lengths are slightly longer than those found from experiments. This indicates that the BLYP method slightly exaggerated electron correlation effect while the HF theory neglected this effect. The results of B3P86/6-31G\* and B3LYP/6-31G\* are in good agreement with the experimental values. Therefore B3LYP and B3P86 methods are superior to BLYP method in the geometry optimization. The atom numbering for the compounds is shown in Fig. 1. From Fig. 1., we can see the three skeletal nitrogen atoms are approximately linear, but the hydrogen atom of HN<sub>3</sub> and

the carbon atom of CH<sub>3</sub>N<sub>3</sub> are not on the axis of the skeletal atoms.

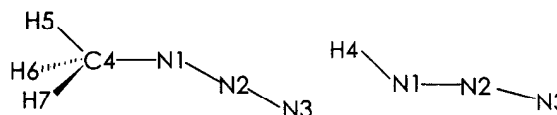


Fig. 1 Geometries of CH<sub>3</sub>N<sub>3</sub> and HN<sub>3</sub>.

### Frequencies

Hydrazoic acid is a planar molecule belonging to the *C<sub>s</sub>* point group. There are five frequencies belonging to species A' and only one frequency belongs to the species A''. Similarly, the methyl azide also belongs to *C<sub>s</sub>* point group. Ten symmetry coordinates belong to species A' and five symmetry coordinates belong to species A''. The calculated frequencies and the experimental frequencies<sup>10-14</sup> are given in Tables 1-4 for HN<sub>3</sub>, DN<sub>3</sub>, CH<sub>3</sub>N<sub>3</sub> and CD<sub>3</sub>N<sub>3</sub>. The mean absolute deviation and standard deviation between the calculated harmonic and the experimental vibrational frequencies for each method are also given in these Tables. Mode descriptions given in these Tables are based on the BLYP force field. In order to investigate the performance and limits of different DFT methods in predicting the vibrational frequencies, overall mean absolute deviation and standard deviation are given in Table 5.

Results in Tables 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<sup>-1</sup> for B3LYP, 69.4 and 100.0 cm<sup>-1</sup> for B3P86. The other three DFT methods, BLYP, LSDA and BP86, yield a much higher level of conformity between the calculated results and the experimental vibrational frequencies. The overall mean absolute and standard deviations are 29.1 and 38.8 cm<sup>-1</sup> with the BLYP results, 51.5 and 74.7 cm<sup>-1</sup> with the LSDA results, 14.2 and 53.1 cm<sup>-1</sup> with the 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 being slightly smaller.

**Table 1** Calculated and experimental fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{HN}_3$ 

Sym.	Exp. <sup>a</sup>	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 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	

<sup>a</sup> Experimental frequencies are obtained from Ref. 14.**Table 2** Calculated and experimental fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{DN}_3$ 

Sym.	Exp. <sup>a</sup>	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 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	

<sup>a</sup> Experimental frequencies are obtained from Ref. 14.**Table 3** Calculated and experimental fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of  $\text{CH}_3\text{N}_3$ 

Sym.	Exp. <sup>a</sup>	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	3023m	3089	3096	3113	3174	3192	3329	3248	Asym. $\text{CH}_3$ str.
A''	2962m	3012	3020	3034	3098	3117	3258	3186	Sym. $\text{CH}_3$ str.
A'	2935m	2957	2958	2968	3038	3050	3200	3101	Asym. $\text{CH}_3$ str.
A'	2106vs	2149	2186	2299	2264	2300	2474	2375	Asym. NNN str.
A''	1538m	1483	1474	1458	1523	1519	1643	1553	$\text{CH}_3$ wag.
A'	1447s	1482	1473	1455	1521	1517	1641	1557	Asym. $\text{CH}_3$ def.
A'	1417s	1432	1424	1422	1474	1472	1602	1498	Sym. $\text{CH}_3$ def.
A'	1272vs	1285	1313	1394	1349	1380	1388	1335	Sym. NNN str.
A'	1132m	1132	1123	1119	1115	1159	1269	1175	$\text{CH}_3$ rock
A''	1036vs	1085	1080	1078	1120	1119	1223	1147	$\text{CH}_3$ 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	$\text{CH}_3$ torsion
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	

<sup>a</sup> Experimental frequencies are obtained from Ref. 10.

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

The calculated harmonic frequencies of HF and MP2 methods at 6-31G\* basis set also listed in Tables 1–4. As we can see, The worst agreement between the calculated and experimental results is found with HF/6-31G\* results. There is a large overestimation of the frequencies at HF level, which may be due to the slightly too short bond lengths resulting from neglecting electron correlation in the HF theory. Even considering the scale factors, the results are still worse than those of DFT methods. At MP2/6-31G\* level, the larger deviations are also found compared with those of five DFT meth-

ods. According to Ref. 15, the overall mean absolute deviation and standard deviation between experimental and calculated frequencies are 154.4 and 204.9 cm<sup>-1</sup> for HF/6-31G\*\*, 99.2 and 132.3 cm<sup>-1</sup> for MP2/6-31G\*\*. Though enlarging the basis set level, the results are not improved, which implies 6-31G\* basis set is a relatively reliable one for the computation of these compounds. From the above discussion, we can conclude that DFT is the relatively superior method for predicting vibrational frequencies.

**Table 4** Calculated and experimental fundamental vibrational frequencies (cm<sup>-1</sup>) of CD<sub>3</sub>N<sub>3</sub>

Sym.	Exp. <sup>a</sup>	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2	Assignment
A'	2379vw	2289	2313	2294	2353	2366	2483	2413	Sym. CD <sub>3</sub> str.
A''	2226m	2235	2291	2240	2298	2313	2418	2365	Asym. CD <sub>3</sub> str.
A'	2118vs	2151	2250	2185	2263	2299	2467	2369	Asym. NNN str.
A'	2074s	2118	2131	2120	2178	2188	2296	2223	Asym. CD <sub>3</sub> str.
A''	1285s	1285	1412	1317	1351	1384	1186	1123	Sym. NNN str.
A'		1071	1047	1063	1099	1095	1234	1144	Asym. CD <sub>3</sub> def.
A'		1068	1042	1059	1095	1091	1185	1123	CD <sub>3</sub> rock
A'	945m	911	938	916	949	957	1053	957	CD <sub>3</sub> rock
A''		834	849	833	862	863	942	881	CD <sub>3</sub> rock
A'	830w	815	835	826	851	826	916	859	CN str.
A''	560w	535	569	542	573	580	668	551	NNN bend
A'	231	222	220	222	230	229	256	215	CNNN bend
A''	90w	83	72	82	79	78	86	112	CD <sub>3</sub> torsion
Mean abs. dev.		24.8	42.0	28.3	41.0	48.9	138.2	90.7	
Standard dev.		35.7	64.7	39.1	62.9	77.7	178.6	131.9	

<sup>a</sup>Experimental frequencies are obtained from Ref. 10.

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

**Table 5** Overall mean deviations, mean absolute deviations, and standard deviations (cm<sup>-1</sup>)

	BLYP	LSDA	BP86	B3LYP	B3P86	HF	MP2
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

Even though B3LYP is superior to BLYP for many properties, the fact that the BLYP frequencies are closer to experimental fundamental vibrational frequencies has important implications for interpreting observed vibrational spectra. As discussed by Rauhut and Pulay, the high level of conformity between BLYP results and the observed fundamental frequencies may be due to error cancellation. Our geometry optimization indicates that

due to slight exaggeration of electron correlation by BLYP method, the BLYP bond lengths are slightly longer than the corresponding B3LYP bond distances. The BLYP force constants and vibrational frequencies are therefore slightly smaller than the corresponding B3LYP results. As the effect of anharmonicity is also to lower the vibrational frequencies, the high level of conformity between BLYP harmonic frequencies and the ob-

served results is likely to be attributable to overestimation of the bond length by the BLYP method. Comparisons between the experimental infrared spectrum of  $\text{HN}_3$  and theoretical infrared spectra and intensities simulated from the BLYP are given in Fig. 2. Agreement between the experimental and simulated spectral features indicates that the BLYP infrared intensities are qualitatively correct. A noticeable difference between them is that the 3250, 2402, 2304 and 950  $\text{cm}^{-1}$  bands in the experimental spectrum do not appear in the theoretical spectra. We think that these bands are not the fundamental vibrational frequencies and the 3250, 2402 and 950  $\text{cm}^{-1}$  bands are combination vibrations of the NH stretch and NNN stretch, the 2304  $\text{cm}^{-1}$  is the multiplying vibration of NNN stretch. Therefore, the high level of conformity between the observed and calculated spectral features indicates that BLYP, without any empirical adjustment, probably, can be used as a more straightforward and practical approach to deduce the observed fundamental vibrational frequencies for many molecules whose vibrational spectra are not well understood.

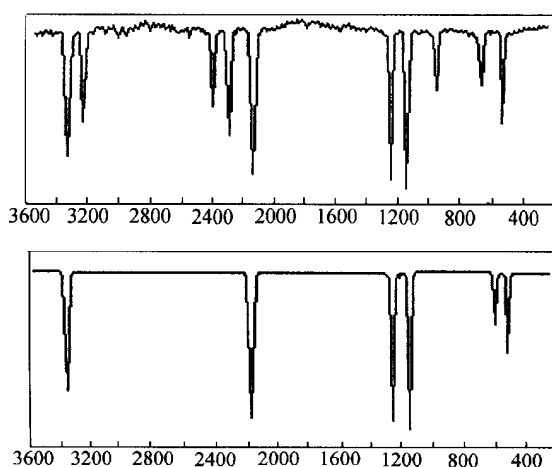


Fig. 2 Comparison of the experimental (upper) and the BLYP/6-31G\* (lower) infrared spectra of  $\text{HN}_3$ .

#### *Effect of the isotope*

#### *Hydrazonic acid*

We investigated the changes in the infrared spectral features for the isotopomer relative to the neutral non-deuterated  $\text{HN}_3$ . On deuteration to form  $\text{DN}_3$ , the normal mode frequencies for NH stretch, NNNH bend, and

NNN stretch are lowered. The largest isotopic effects in  $\text{HN}_3$  molecule appear on the NH stretch, which has decreased by about 850  $\text{cm}^{-1}$  due to the deuterio-substitution. The BLYP calculated values are lowered by 890  $\text{cm}^{-1}$  which is in excellent agreement with the experimental shifts. The NN stretch and NNN outer plane bending changed very little. The BLYP calculated values of the shifts confirm this fact.

#### *Methyl azide*

For methyl azide the effect of deuterio-substitution on vibrational frequencies is identical with that for hydrazonic acid. For  $\text{CH}_3\text{N}_3$  molecule, the main effects in frequency appear on the symmetric  $\text{CH}_3$  stretch, asymmetric  $\text{CH}_3$  stretch,  $\text{CH}_3$  rock and  $\text{CH}_3$  torsion. The largest effects in  $\text{CH}_3\text{N}_3$  molecule appear on the  $\text{CH}_3$  stretch, which has decreased by about 720  $\text{cm}^{-1}$  due to the deuterio-substitution. The BLYP calculated values of the shifts also confirm this fact. The NNN bend, NNN asymmetry stretch and NNN symmetry stretches remain effectively unchanged in frequency.

In addition, the substitution of the hydrogen in  $\text{HN}_3$  by a methyl group causes a great change of NNN stretches while has little effect on  $\text{N}(2)\text{N}(3)$  stretches. The reason is that neither  $\text{CH}_3$  nor H has a significant effect on terminal nitrogen atoms  $\text{N}(2)\text{N}(3)$ . Therefore the frequencies mainly related to  $\text{N}(2)\text{N}(3)$  bond vibration in  $\text{CH}_3\text{N}_3$  must change little. On the other hand, both  $\text{CH}_3$  and H have a significant effect on the central nitrogen atoms  $\text{N}(1)$  and  $\text{N}(2)$ , so the frequencies related to the central  $\text{N}(1)\text{N}(2)$  bond vibration must change a large amount. The former discussion is in good agreement with the Ref. 15.

## Conclusion

We have carried out DFT and HF, MP2 calculations on the structures and vibrational frequencies of hydrazonic acid and methyl azide molecules and their isotopomers. Comparison between calculated and experimental results indicates that B3LYP is superior to BLYP for the geometry optimization, while the BLYP frequencies are closer to experimental fundamental vibrational frequencies. It is found that using BLYP DFT reproduces the observed fundamental vibrational frequencies

very well with the overall mean absolute deviations about  $29.1\text{ cm}^{-1}$  and standard deviations about  $38.8\text{ cm}^{-1}$  between the calculated and experimental results. This accuracy is desirable for resolving disputes in vibrational assignments and provides valuable insight for understanding the observed spectral features.

Therefore, it is a promising approach for identifying an unknown compound by comparing its vibrational spectrum with calculated results of a few candidates and the BLYP calculated results may be served as a guide for a further experimental search for the missing fundamentals of the target molecule. Furthermore, since the DFT results without any empirical adjustment can be compared directly with experimental results, it will gain more and more popularity in the calculation of vibration frequencies.

## References

1. Parr, R. G.; Yang, W., *Density Functional Theory of Atoms and Molecules*, Oxford, New York, 1989.
2. Jones, R. O.; Gunnarsson, O., *Rev. Mol. Phys.*, **61**, 689(1989).
3. Ziegler, T., *Chem. Rev.*, **91**, 651(1991).
4. Kohn, W.; Sham, L., *J. Chem. Phys.*, **A140**, 11133(1965).
5. Handy, N. C.; Murray, C. W.; Amos, R. D., *J. Phys. Chem.*, **97**, 4392(1993).
6. Chong, D. P.; Bree, A. V., *Chem. Phys. Lett.*, **210**, 443(1993).
7. Zhou, X. F.; Krauser, J. A.; Tate, D. R.; Vanburen, A. S.; Clark, J. A.; Moody, P. R.; Liu, R. F., *J. Phys. Chem.*, **100**, 16822(1996).
8. Johnson, B. G.; Gill, P. M. W.; Pople, J. A., *J. Chem. Phys.*, **98**, 5612(1993).
9. Rauhut, G.; Pulay, P., *J. Phys. Chem.*, **99**, 3093(1995).
10. Eyster, E. H.; Gillette, R. H., *J. Chem. Phys.*, **8**, 369(1940).
11. Pierson, R. H.; Fletcher, A. N.; Gantz, E. St. C., *Anal. Chem.*, **28**, 1232(1956).
12. Mantca, E.; Zerbi, G., *Gazz. Chim. Ital.*, **90**, 53(1960).
13. Miller, F.; Bassi, A. D., *Spectrochim. Acta*, **19**, 565(1964).
14. Dows, D. A.; Pimentel, G. C.; *J. Chem. Phys.*, **23**, 1258(1955).
15. Wang, Z. Z., *J. Mol. Struct. (Theochem.)*, **434**, 1(1998).
16. Slater, J. C., *Quantum Theory of Molecules and Solids*, Vol. 4, McGraw, New York, 1974.
17. Vosko, S. H.; Wilk, L.; Nusair, M., *Can. J. Phys.*, **58**, 1200(1980).
18. Becke, A. D., *Phys. Rev.*, **A38**, 3098(1988).
19. Lee C.; Yang, W.; Parr, R. G., *Phys. Rev.*, **B37**, 785(1988).
20. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H., *Chem. Phys. Lett.*, **157**, 200(1989).
21. Perdew, J. P., *Phys. Rev.*, **B33**, 8822(1986).
22. Becke, A. D., *J. Chem. Phys.*, **98**, 5648(1993).
23. Florian, J.; Johnson, B. G., *J. Phys. Chem.*, **98**, 3681(1994).
24. Winnewser, M.; Cook, R. L., *J. Chem. Phys.*, **41**, 999(1996).
25. Livingston, R. L.; Tao, C. N. R., *J. Phys. Chem.*, **64**, 756(1960).

(E9908111 ZHOU, X. M.; LING, J.)