Theoretical Prediction of Infrared Spectra and Thermodynamic Properties of Glyceryl Nitrates[*]

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[**ABSTRACT**]　Glyceryl nitrates are one type of compounds with wide applications in military, medicine, etc. In this study, 6 glyceryl nitrates including NG, DGTN, DGPN, DGHN, TriGPN, and TetraGHN were investigated at the B3LYP/6-31G* level of density functional theory. The infrared spectra were obtained and assigned. The frequencies scaled by a factor of 0.96 were then used to calculate the thermodynamic properties based on the principle of statistic thermodynamics. The thermodynamic properties are correlated with the number of —ONO_2 and —CH_2—O—CH_2—CH(ONO_2)— groups in a linear manner, obviously showing a good group additivity character.

[**KEYWORDS**]　glyceryl nitrates; IR spectra; thermodynamic properties; density functional theory

[**CLASSIFICATION CODE**]　TQ560. 71;O64

甘油硝酸酯类化合物红外光谱和热力学性质的理论研究

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[摘　要]　甘油硝酸酯类化合物广泛应用在军事、医学等方面。用密度泛函理论方法, 在 B3LYP/6-31G* 水平下, 对 NG、DGTN、DGPN、DGHN、TriGPN 和 TetraGHN 6 种甘油硝酸酯类化合物进行了研究, 获得它们的红外光谱并作归属。对谐振频率以 0.96 进行标度, 基于统计热力学原理, 计算了它们的热力学性质。热力学性质与硝酸酯基和—CH_2—O—CH_2—CH(ONO_2)—基之间具有线性关系, 表现出很好的基团加和性。

[关键词]　甘油硝酸酯;红外光谱;热力学性质;密度泛函理论

Introduction

Solid propellants are the propulsion power behind rockets, missiles and launch vehicles. They are generally a type of high energy composite materials, which eject as hot gaseous products on combustion from the nozzle to produce forward thrust to propulsion units. Properties of propellants play an important role in the development of aerospace industry and the survival capacity and combat efficiency of missiles. An ongoing effort in energetic materials community is to design new propellants with high performance and desirable mechanical and safety properties. Such properties are adjustable via formulations of oxidizers, plasticizers, metallic fuels, polymer binders, and other high energy additives. Nitrate ester is an important kind of organic compounds with excellent plasticizing properties and

widely used as components of industrial explosives (dynamites) and smokeless powders. One of the oldest classes of fielded energetic materials used both in gun and rocket propellants, is based on various stocks of nitrocellulose (NC) and plasticized most often with nitroglycerine (NG)[1-3]. Methyl nitrate (MN), ethylene glycol dinitrate (EGDN), pentaerythritol tetranitrate (PETN), etc., have also been receiving a lot of investigations[4-21]. EGDN, diethylene glycol dinitrate (DEGDN), NG, etc., have been paid considerable attentions in synthesis and analysis. Their structures, heats of formation, pyrolysis mechanism, mechanical properties, etc., have been studied theoretically by the semi-empirical molecular orbital (MO) method, ab initio MO method, density functional theory (DFT), and molecular dynamics (MD), etc. Vibrational spectra and thermodynamic properties of some nitrates have been studied by using ab initio or density functional methods[12-13,15,18,20]. However, previous studies on some of nitrate esters little involve polyglycerine polynitrates to systematically study their IR spectra and thermodynamic properties. IR spectrum, as is well known, is not only the basic property of compounds, but also an effective measure to analyze substances. Therefore, it is of great importance to predict IR spectra for both theoretical and practical reasons. Thermodynamic properties, such as heat capacity, entropy, and enthalpy, are important parameters for compounds and are necessary in predicting reactive properties of chemical reactions at different temperatures. Accurate prediction of thermodynamic properties is important in developing models for chemical reactions in which experimental

data are incomplete or inaccurate. For example, based on thermodynamic properties, accurate prediction of $\triangle_f H_m^\theta$ can be achieved and help us predict detonation properties of explosives[22].

Studies[13,15,20,23] have shown that the DFT-B3LYP method[24-25] in combination with the 6-31G*[26] basis set is able to produce accurate molecular structures, infrared vibrational frequencies, and thermodynamic properties[15]. Therefore, in this paper, 6 glyceryl nitrates (such as NG, DGTN, DGPN, DGHN, TriGPN and TetraGHN, see Fig. 1) are studied using this DFT method. Their IR spectra are assigned by the vibrational analysis and vibrational frequencies are used to evaluate thermodynamic parameters according to the statistical thermodynamic theory. The results of this study can be helpful for further studies on other physical, chemical, and energetic properties of these compounds.

1　Computational Methods

Six glyceryl nitrates are studied at the B3LYP/6-31G* level with the Gaussian 03 program package. Since the DFT-calculated harmonic vibrational frequencies are usually larger than the experimentally observed values, they are scaled using a factor of 0.96 as was done before[27]. On the basis of the principle of statistical thermodynamics[28], standard molar heat capacity ($C_{p,m}^o$), standard molar entropy (S_m^o), and standard molar enthalpy (H_m^o) from 200 to 800 K are derived using a self-compiled program.
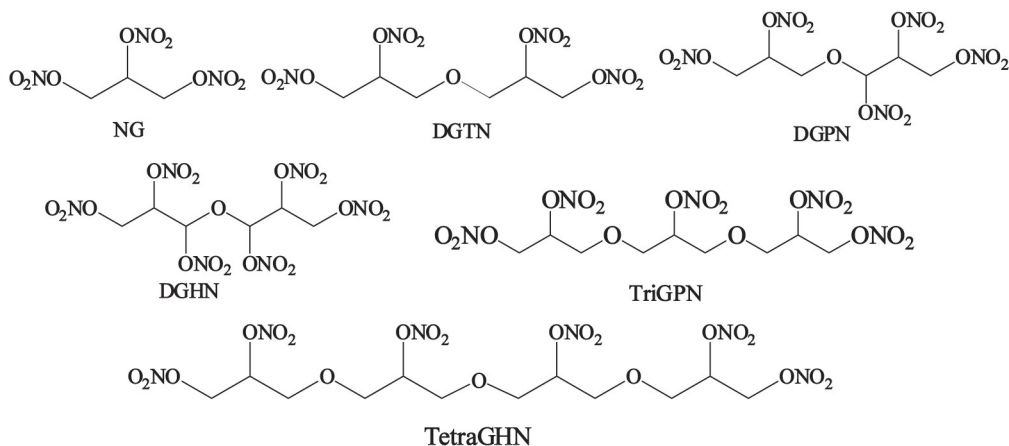

Fig. 1　Illustration of the molecular structures of glyceryl nitrates

2　Results and discussion

2.1　Infrared spectra

　　Vibrational analysis is necessary as a part of theoretical prediction of thermodynamic properties and can provide the motions responsible for the vibrational modes. Tab. 1 presents the calculated IR spectra of the glyceryl nitrates. Due to the complexity of vibrational modes, the vibrational spectra of the title compounds are difficult to be completely assigned, therefore, only some typical vibrational modes are analyzed and discussed.

　　Tab. 1 shows that, the calculated frequencies of NG are closed to the values in Ref. [3], e. g. the calculated frequencies (812.4-833.6, 1 271.9-1 278.9, 1 696.9-1 703.2 cm^{-1}) are in accord with the experimental values (842.0, 1 276.0 and 1 651.0 cm^{-1}). This demonstrates the dependability of theoretical computation results. The trivial discrepancy is perhaps due to the intermolecular interactions existed in experimental samples.

　　Data in Tab. 1 show that there are three main characteristic regions. There are two intense characteristic peaks in their IR spectra. One is in 1 684.2-1 728.3 cm^{-1} range, attributed to the N=O asymmetric stretch of —ONO$_2$ groups. In this region, their cen-

tral positions move towards higher frequency as the number of —ONO$_2$ groups increases. For instance, the vibration frequencies of DGTN, DGPN and DGHN are 1 698.9-1 713.1, 1 706.1-1 723.6 and 1 704.1-1 728.3 cm^{-1}, respectively. Moreover, their central positions also basically move towards higher frequency as the number of —CH$_2$—O—CH$_2$—CH(ONO$_2$)— increases. Besides, the difference between the frequencies of the isomers is small, indicating that the straight chain length, the space orientation of groups, and the branch chain have little influences on frequencies. Another intense band locates at 1 271.9-1369.4 cm^{-1}, corresponding to the N=O symmetric stretch of —ONO$_2$ groups and out of plane bend of C—H bonds. In this region, the main frequencies increase with the increasing number of —CH$_2$—O—CH$_2$—CH(ONO$_2$)— groups, but with the increase of —ONO$_2$ groups, the main frequencies may increase and decrease. Finally, the weak peaks at less than 1 129.0 cm^{-1} are mainly caused by the stretching vibration of O—NO$_2$, C—ONO$_2$ and C—O(CH$_2$) bonds, which belongs to the fingerprint region and can be used to identify isomers.

2.2　Thermodynamic properties

　　Thermodynamic properties of the title compounds ranging from 200 to 800 K are calculated and presented in Tab. 2.

Tab. 1　Key vibrational frequencies of glyceryl nitrates computed at the B3LYP/6-31G* level[a]

cm^{-1}

Compound	ν_s(O—NO$_2$)	ν_s(C—O)	ν_s(N=O) and ν_b(C—H)	ν_{as}(N=O)
NG	812.4, 816.1, 833.6 (842.0)[b]	887.5, 997.3	1 271.9, 1 278.9 (1 276.0)[b]	1 696.9, 1 697.7, 1 703.2 (1 651.0)[b]
DGTN	806.5, 813.2, 823.6	880.4, 992.0, 1 138.0	1 274.6, 1 296.1, 1 303.3	1 698.9, 1 703.3, 1 706.1, 1 713.1
DGPN	791.4, 797.7, 822.0	953.3, 1 003.1, 1 126.4	1 288.3, 1 296.4, 1 313.0	1 706.1, 1 708.3, 1 718.2, 1 723.6
DGHN	772.4, 789.3, 797.0, 817.4	956.7, 982.9, 1 000.9, 1 113.0	1 282.3, 1 288.5, 1 290.1, 1 309.0, 1 311.6, 1 318.0	1 704.1, 1 708.2, 1 722.5, 1 726.1, 1 728.3
TriGPN	809.5, 811.9, 825.0, 838.9	894.2, 1 001.1, 1 011.4, 1 129.0	1 282.1, 1 282.4, 1 285.7, 1 290.4, 1 364.2	1 684.2, 1 697.1, 1 717.2
TetraGHN	818.1, 821.9, 841.1	869.4, 894.7, 1 005.8, 1 012.8, 1 123.0	1 278.9, 1 279.1, 1 286.8, 1 294.9, 1 369.4	1 689.1, 1 697.2, 1 697.3, 1 712.3

a, ν_s(O—NO$_2$): O—NO$_2$ stretch; ν_s(C—O): C—ONO$_2$ and C—O(CH$_2$) stretches; ν_s(N=O) and ν_{as}(N=O): N=O symmetric and asymmetric stretches of nitro groups; ν_b(C—H): C—H out of plane bend. b, values taken from Ref [3] are in parentheses.

Tab. 2　Thermodynamic properties of the title compounds at different temperatures[a]

Compounds	para-meters	T/K							
		200.00	298.15	300.00	400.00	500.00	600.00	700.00	800.00
NG	$C_{p,m}^{o}$	163.39	214.55	215.49	262.21	300.25	330.21	353.78	372.55
	S_{m}^{o}	459.49	534.31	535.64	604.22	666.98	724.48	777.22	825.73
	H_{m}^{o}	−958.038	−958.031	−958.031	−958.022	−958.011	−957.999	−957.986	−957.972
DGTN	$C_{p,m}^{o}$	261.08	342.34	343.84	420.56	484.55	535.73	576.50	609.32
	S_{m}^{o}	631.70	751.09	753.21	862.89	963.86	1 056.90	1 142.66	1 221.86
	H_{m}^{o}	−1 430.757	−1 430.746	−1 430.746	−1 430.731	−1 430.714	−1 430.695	−1 430.673	−1 430.651
DGPN	$C_{p,m}^{o}$	300.59	393.75	395.45	480.46	549.92	604.69	647.82	682.15
	S_{m}^{o}	684.69	822.19	824.64	950.38	1 065.35	1 170.65	1 267.23	1 356.06
	H_{m}^{o}	−1 710.429	−1 710.416	−1 710.416	−1 710.399	−1 710.379	−1 710.357	−1 710.333	−1 710.308
DGHN	$C_{p,m}^{o}$	340.92	445.73	447.61	540.64	615.42	673.73	719.19	755.05
	S_{m}^{o}	752.42	908.34	911.10	1 053.03	1 182.03	1 299.61	1 407.02	1 505.49
	H_{m}^{o}	−1 990.101	−1 990.086	−1 990.086	−1 990.067	−1 990.045	−1 990.020	−1 989.994	−1 989.966
TriGPN	$C_{p,m}^{o}$	358.91	468.72	470.79	577.40	667.57	740.24	798.45	845.50
	S_{m}^{o}	816.77	980.42	983.32	1 133.67	1 272.54	1 400.92	1 519.56	1 629.36
	H_{m}^{o}	−1 903.477	−1 903.462	−1 903.462	−1 903.442	−1 903.418	−1 903.391	−1 903.362	−1 903.330
TetraGHN	$C_{p,m}^{o}$	454.65	595.05	597.71	734.84	851.29	945.39	1 020.92	1 082.08
	S_{m}^{o}	976.17	1 183.69	1 187.38	1 378.49	1 555.40	1 719.24	1 870.86	2 011.31
	H_{m}^{o}	−2 376.195	−2 376.176	−2 376.175	−2 376.150	−2 376.120	−2 376.085	−2 376.048	−2 376.008

a, Units: $C_{p,m}^{o}$: J/(mol·K); S_{m}^{o}: J/(mol·K); H_{m}^{o}: a.u.

Tab. 2 shows that all the thermodynamic functions increase evidently with the rise of temperature. The reasonable interpretation of this result is that translational, vibrational and rotational movements strengthen as the temperature increases, so the thermodynamic functions H_{m}^{o} and S_{m}^{o}, contributed from these three movements, increase evidently. As for translational $C_{p,m}^{o}$ and rotational $C_{p,m}^{o}$, they are constant under some approximations. Only vibrational heat capacity depends on temperatures. The vibrational movement is weak when temperature is low, so the main contributions to $C_{p,m}^{o}$ come from the translation and rotation of molecule, while with the rise of the temperature, the vibrational movement is intensified and therefore makes more contributions to $C_{p,m}^{o}$, which leads to the increase in $C_{p,m}^{o}$ values.

In addition, $C_{p,m}^{o}$ and S_{m}^{o} linearly increase with the number of —ONO_2 groups and —CH_2—O—CH_2—CH(ONO_2)— groups (NG, DGTNa, TriGPNa, TetraGHNa, $n = 0, 1, 2, 3$), while H_{m}^{o} linearly decreases. Fig. 2 provides the linear relations between the substituent number of —CH_2—O—CH_2—CH(ONO_2)— (n) and the calculated thermodynamic functions at

298.15 K, respectively. The correlation coefficients are all bigger than 0.998 9. On this condition, $C_{p,m}^{o}$, S_{m}^{o}, and H_{m}^{o} change on average by 126.79 J/(mol·K), 217.75 J/(mol·K), and −472.72 kJ/mol, respectively when more —CH_2—O—CH_2—CH(ONO_2)— groups are introduced.

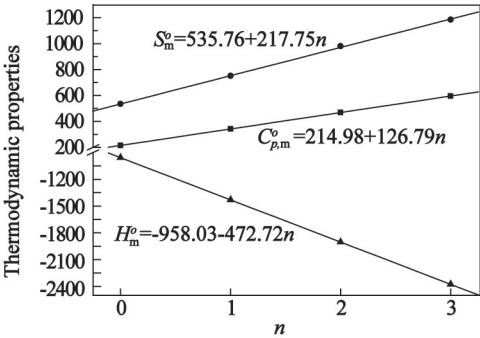Fig. 2　Relationships between the thermodynamic functions and the number of —CH_2—O—CH_2—CH(ONO_2)— (n) at 298.15 K

3　Conclusions

From theoretical calculations and analyses of the IR spectra and thermodynamic properties of glyceryl ni-

trates at the B3LYP/6-31G* level, the following conclusions are drawn:

1) The calculated and assigned IR spectra have three strong characteristic regions. Two of them correspond to the N=O asymmetric and symmetric stretches of the —ONO$_2$ groups and the out of plane bend of the C—H bonds. The third mainly corresponds to the stretching vibration of the O—NO$_2$, C—ONO$_2$ and C—O(CH$_2$) bonds;

2) Thermodynamic properties in the range from 200 to 800 K are calculated. All the thermodynamic fuctions increase evidently with the rise of temperature.

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