Investigation of Electronic Structural, Thermodynamic Properties, Spectroscopic Analysis (FT-IR, FT-RAMAN, UV-Vis) of Nitromethane

Rinku Sharma*, Manuj Ahuja*** and Sanjay Gulia**

Department of Applied Physics, Delhi Technological University, Delhi-110042, India
*** Instruments Research and Development Establishment, DRDO, Dehradun-248008, India*
***Corresponding Author: manujahuja_2k19mscphy04@dtu.ac.in*

ABSTRACT

In the present work, the computational investigation of Electronic molecular structural, Thermochemistry, Spectroscopical analysis: (FT-IR, FT-RAMAN, UV-Vis) of Nitromethane (CH3NO2) are performed by Gaussian and the calculations are compared with the existing experimental and theoretical data available for the molecule. Optimized structure, fundamental scaled and unscaled vibrational frequencies, Mulliken charges are modeled using HF method, DFT (Density Functional Theory), and different basis sets. Study of thermodynamic functions: partition function, thermal energy, entropy, and specific heat capacity of the Nitromethane as a function of temperatures and MEP (molecular electrostatic potential) are obtained using density functional theory, B3LYP/ Basis Set-1 (6-311++G(d,p)). The B3LYP/ Basis Set-1 (6-311++G(d,p)) basis sets calculations used here matches well with the experimental infrared spectra data over the other calculations. The oscillator strength and energy calculations alongwith spectroscopic analysis in terms of UV-Visible spectrum on the optimized structure of Nitromethane using TD-DFT, time-dependent DFT are performed in this paper.

Keywords: Nitromethane; DFT; B3LYP; HF; UV; FT-IR, RAMAN; MEP; Thermodynamic properties.

1. INTRODUCTION

Nowadays, computational chemistry [1] helps to provide new insight and allows molecular structure calculations using many quantum chemical numerical methods [2-6] even in the absence of availability of experimental data. Extensive theoretical studies exist for calculating electronic structural and spectroscopic properties using computational molecular modeling [4]. DFT (density functional theory) method [5-6] is an effective and efficient computational Quantum chemical methods widely used in recent years, as it provides accurate results for optimized geometry, dipole moment, atomic charges, vibrational frequencies, excitation energies, molecular electrostatic potential, thermodynamical parameters [7-10] when compared to experimental values.

Nitromethane is an organic polar nitro compound with the chemical formula CH3NO2, has been the subject of research investigations globally as it has various industrial and research applications [11]. It is used as a precursor of high-energy material [12]. The Nitromethane may affect the atmosphere adversely but the concentration in the environment is too low to have harmful effects [13]. It is used to manufacture the industrial antimicrobials and pharmaceuticals [14] and is also used as a fuel for rockets and radio-controlled models [15]. It has been observed that Nitromethane can be used effectively as a propellant which gives high combustion performance and the burning behavior. The studied molecule has one NO2 that offers a distinctive spectral feature in many high explosives. Owing to its explosive nature and causing atmospheric pollution, the flame spectrum in the UV-Visible spectral range for CH3NO2 [16] and thermal decomposition of nitromethane for different pressure conditions [17] have also been studied. It became important to understand and analyze deeply the behavior this molecule in terms of Gas- Phase Acidity, electron Affinity,

Negative Ion States, Bond Dissociation Energy [18], gas-phase solvation processes [19], Gas-phase decomposition mechanisms [20] and explosive nature [21]. As reported in literature, up to the knowledge of authors, the accurate data for complete HOMO/LUMO and Dipole moment analysis for gas phase and by adding different solvents phases of Nitromethane was calculated using different computational methods [22]. Whereas very few theoretical studies and experimental results are available for spectroscopic analysis and thermodynamic behavior.

In this research paper, we report the molecular optimized structure, electronic, thermodynamical properties at different temperatures, molecular geometry, range of wavenumbers and UV-Visible spectral analysis for Nitromethane. Our results extended to calculate various parameters such as electronic transition energy, oscillation strength, thermodynamical parameters, and their behavior as a function of temperature. UV-Visible spectrum, Molecular electrostatic potential, Mulliken charges, etc. The attempted detailed assignments of vibrational frequencies were made and it introduced a scaling factor in frequencies to values which testifies the experimental data available.

2. EXPERIMENTAL DETAILS

The Fourier Transform-RAMAN experimental spectrum of the molecule was recorded using PREEMPTOR system developed by Defence Research and Development Organization (DRDO), Delhi, India. The spectra of the molecule have been recorded experimentally using LASER excitation wavelength 532 nm with resolution of 8 cm-1. The Raman spectra has been integrated for 2 seconds.

3. COMPUTATIONAL DETAILS

The infrared spectrum IR of the Nitromethane was taken from the Reference Data of the National Institute of Standards and Technology, NIST [23]. The experimental IR spectrum database for the gaseous phase [24] and the liquid phase [25, 26] was taken from the research articles published.

Quantum chemical computations for Nitromethane using the Gaussian program involving the molecular orbital DFT technique with B3LYP ("Becke, 3-parameter, Lee-Yang–Parr")/ [Basis Set-1 (6-311++G(d,p)) , Basis Set-2 (3-21G), Basis Set-3 (6-311G(d,p))] , and ab-Initio HF (Hartree-Fock) method with Basis Set-1 (6-311++G(d,p)) are used for calculations. The larger and reliable data set levels of theory are selected in such a way so as to have little difference between our calculations and existing experimental values of levels of theory, to understand the complete analysis. The optimization of the molecular structure to the lowest potential was carried out by using these combination basis sets. The procedure on the optimized structure was extended to calculate vibrational frequencies, electronic properties, and UV-Visible spectrum data analysis. After rigorous optimizations, the correct minimum potential energy was found as no imaginary frequency modes were obtained at the optimized geometry. To improve the unscaled frequencies spectrum, a scaling factor was introduced in the calculations. The Vibrational frequencies for the HF method are scaled by 0.92 for the range above 1700 cm-1 and 0.89 for the range below 1700cm. For B3LYP/ (Basis Set-1) are scaled by 0.963 for the range of wavenumber above 1700 cm-1, and below 1700 cm-1 are scaled by 0.98. Gauss View software is used to get visual aid of optimized molecular structure. The Electronic transitions and excited states calculations were performed using larger and more reliable Time-dependent DFT/B3LYP/ (Basis Set-1) to produce the complete data set for Electronic spectrum and excitation energies.

4. RESULTS AND DISCUSSION

4.1. OPTIMIZED MOLECULAR GEOMETRY

The optimized structure form of Nitromethane by DFT/B3LYP/ (Basis Set-1) with atomic numbering is obtained as shown in Fig 1. Molecular geometry is fully optimized with tight convergence criteria, which corresponds to correct energy minima, as only normal modes are obtained at the optimized geometry.The ground state optimized

geometry of the molecule is calculated by larger and accurate simulation basis set B3LYP/ [(Basis Set-1), (Basis Set-2), (Basis Set-3)] and HF/(Basis Set-1) and collated with reported experimental datasets from the literature [27-28].
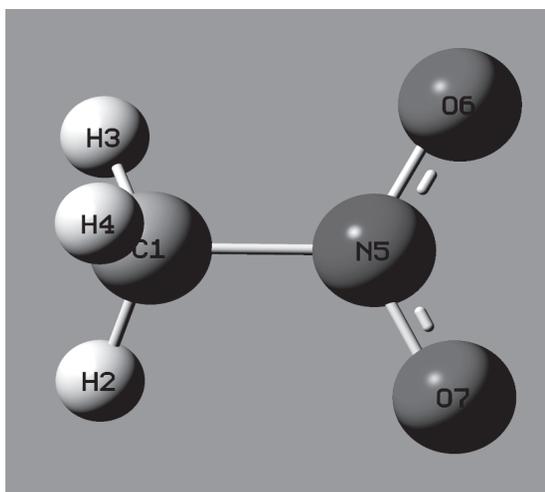

Figure 1. The theoretically optimized geometric molecular structure of Nitromethane.

      This molecule contains one Carbon-Nitrogen bond, two nitrogen-oxygen bonds, and three Carbon-Hydrogen bonds. The calculated values of bond lengths and angles compared with the experimental values as reported in the literature [27-28] are listed in Table 1. The N-O bond lengths are obtained higher by B3LYP/ (Basis Set-2) calculations and lower by HF/(Basis Set-1) calculations. By using the B3LYP/(Basis Set-1), it shows the good match with the experimental and theoretical value as evident from Fig.2.
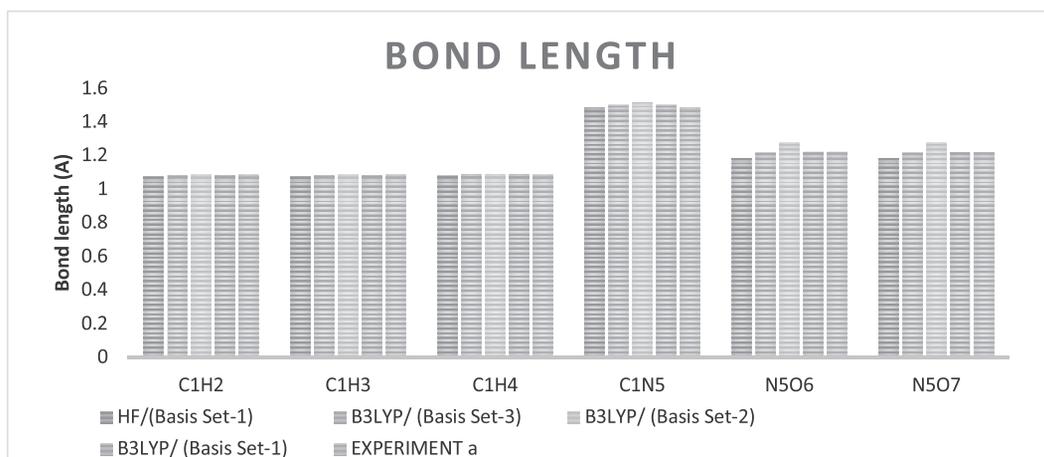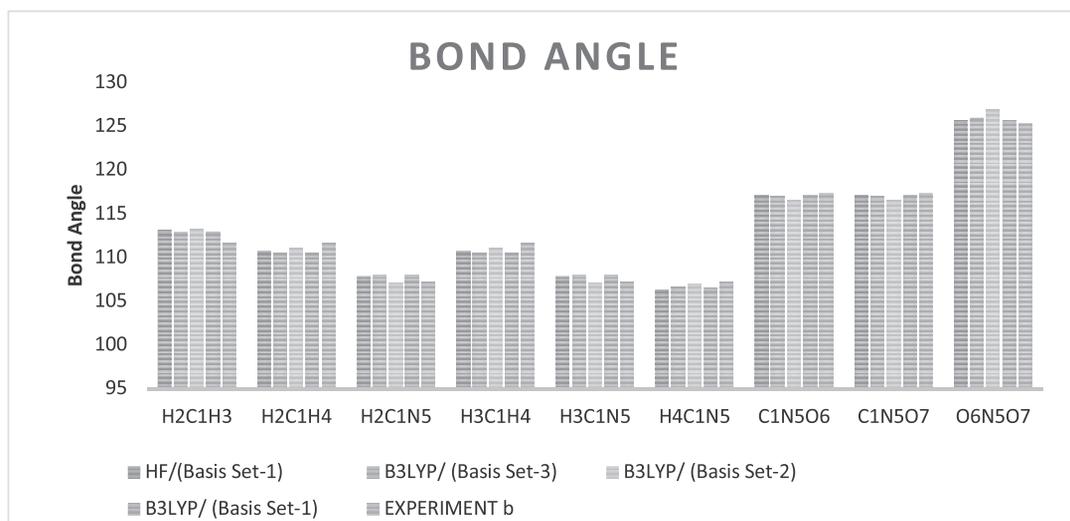
Figure 2. Optimized Structural properties (bond lengths (A) and bond angles (o)) of Nitromethane and also compared with experimental values

4.2. Atomic Charge

Mulliken atomic charges have importance in the application of quantum chemical computational calculations and It effects dipole moment, electronic structure, polarizability, chemical properties of molecular systems. The Mulliken population analysis has been performed to obtain Mulliken atomic charges using Gaussian package. It underlying principle exploits the density–derived electrostatic and chemical (DDEC) techniques to solve this problem by partitioning the electron density to simultaneously reproduce atomic chemical states and the electrostatic potential surrounding the material with excellent accuracy. The distribution of charge is dependent on different basis sets. So these basis sets are used to calculate Mulliken charges as listed in Table 2. The molecular structure charge distribution of nitromethane is shown in Fig 3. The Mulliken atomic charge of all three hydrogen atoms carries a positive charge, The two oxygen atom carries negative charge. The charge of Nitrogen is -0.09817 e- for B3LYP/(Basis Set-1) and 0.052305 e-, 0.236411 e- and 0.239271 e- for HF/(Basis Set-1) , B3LYP/ [(Basis Set-3) and (Basis Set-2). it is shown that the charge of Nitrogen is positive for B3LYP/(Basis Set-1) and negative for HF/(Basis Set-1) and B3LYP/[(Basis Set-3), (Basis Set-2)].

Table 1. Bond length and bond angles of Nitromethane molecule

Bond length		HF Basis Set-1	DFT/B3LYP Basis Set-3	DFT/B3LYP Basis Set-2	DFT/B3LYP Basis Set-1	EXPERIMENT a
R1	C1H2	1.07710	1.0860	1.0867	1.0862	1.0876
R2	C1H3	1.07710	1.0860	1.0867	1.0861	1.0876
R3	C1H4	1.08126	1.0898	1.0916	1.0900	1.0876
R4	C1N5	1.48395	1.5026	1.5168	1.5029	1.4886
R5	N5O6	1.18578	1.2200	1.2775	1.2211	1.2240
R6	N5O7	1.18578	1.2200	1.2775	1.2211	1.2240

Bond Angle	Molecule	HF Basis Set-1	DFT/B3LYP Basis Set-3	DFT/B3LYP Basis Set-2	DFT/B3LYP Basis Set-1	EXPERIMENT b
A1	H2C1H3	113.08133	112.9068	113.2109	112.9473	111.691
A2	H2C1H4	110.71546	110.5091	111.1243	110.5171	111.689
A3	H2C1N5	107.85033	107.9869	107.0188	108.022	107.150
A4	H3C1H4	110.71961	110.5137	111.1282	110.5226	111.689
A5	H3C1N5	107.85248	107.9893	107.0195	108.0247	107.150
A6	H4C1N5	106.30647	106.6743	106.9668	106.5368	107.150
A7	C1N5O6	117.18156	116.9981	116.5057	117.1799	117.331
A8	C1N5O7	117.17880	116.9953	116.5015	117.1764	117.331
A9	O6N5O7	125.61522	125.9770	126.9408	125.6202	125.338

Experiment a - bond lengths were taken from [27]

Experiment b - bond angles were taken from [28]

Table 2. Mulliken atomic charges of nitromethane for different Basis Set

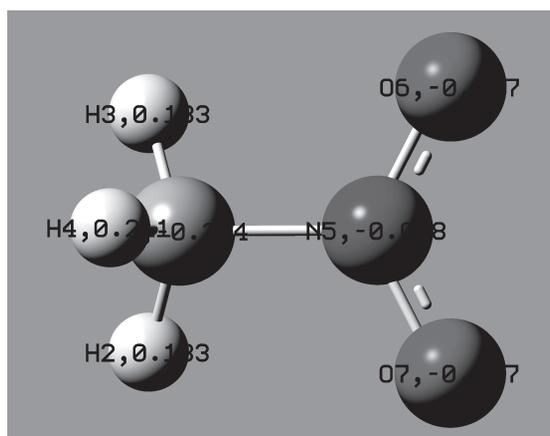| Atoms	`NITROMETHANE			
	HF	Becke, 3-parameter, Lee-Yang–Parr (B3LYP)		
	Basis Set-1	Basis Set-3	Basis Set-2	Basis Set-1
C1	-0.32924	-0.15783	-0.39166	-0.34404
H2	0.180144	0.146717	0.245842	0.182844
H3	0.180101	0.146695	0.245819	0.182793
H4	0.213706	0.159999	0.257046	0.21064
N5	0.052305	0.236411	0.239271	-0.09817
O6	-0.1485	-0.26599	-0.29816	-0.06704
O7	-0.14852	-0.266	-0.29817	-0.06703

Figure 3. The Mulliken atomic charge distribution molecular structure of Nitromethane by using B3LYP/ (Basis-Set-1) large basis set.

4.3. Mep (Molecular Electrostatic Potential)

In the present work, we have plotted a 3D plot of Molecular electrostatic potential Molecular electrostatic potential (MEP) over-optimized geometry in its gas phase as shown in Fig 4. MEP plays a major role in determining the interaction of electrophile on a negative region where the electron density is maximum and neutrophile on a positive region. The utility of MEP Plot is significant when it is visualized through mapping its values on the molecule boundaries shown by reflecting surfaces. In MEP, the Red colour directs the max negative region which shows the region for an electrophilic attack, the Blue colour directs the max positive region which shows the region for nucleophilic attack. The color-grading scheme taken in the mapping of MEP 3D plot is used to identify the size and shape of a molecule and negative, positive, and neutral regions of electrostatic potential. The MEP colour coding ranges between –0.04330 a.u. to 0.04330 a.u. The electronegative atom mainly shows a negative potential region, So nitromethane consists of an electronegative atom, oxygen, and the positive potential is localized over the H atoms can be shown from Fig 4. The negative potential value over oxygen atoms is -0.0395. and compared to this positive potential value over hydrogen atoms is 0.04026. According to these calculations, we can predict that oxygen and hydrogen atoms are the reactive locations for electrophilic and nucleophilic attack resp.
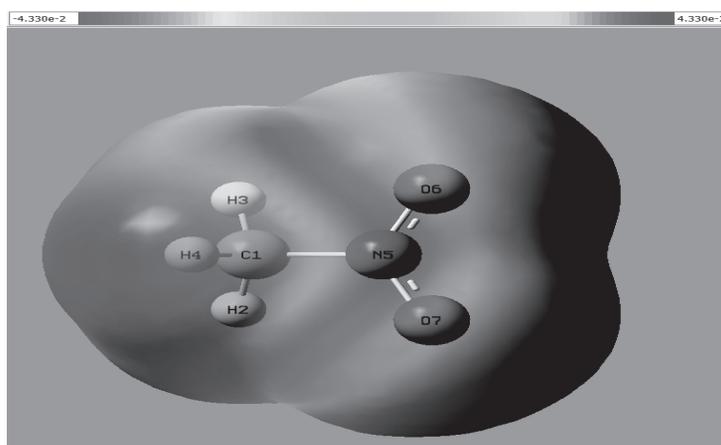

Figure 4. Electrostatic potential mapping of title molecule with atomic numbering

4.4. Thermodynamic Properties

Ab initio Quantum chemical simulations are performed to calculate the thermodynamics functions (zero-point vibrational energy, rotational constants, entropy, specific heat capacity, and dipole moment) of nitromethane in gaseous phase using reliable DFT/B3LYP/[(Basis Set-1), (Basis Set-2), (Basis Set-3)] and HF/(Basis Set-1) method as listed in Table 3. The ground state energy of optimized nitromethane structure found using DFT B3LYP/ (Basis Set-1) is -245 a.u. The ground state energy using HF/ (Basis Set-1) is -243.7 a.u. The numerical difference between these methods is 1.3 a.u. The specific heat and entropy decreases from B3LYP/ [(Basis Set-2) > (Basis Set-3) > (Basis Set-1) while HF method calculates minimum specific heat and entropy among all the basis sets.

The three-dimensional vector, transition dipole moment between the ground state and higher excited states depicts the movement of charge. The dipole moment vector flow direction is primarily from negative to positive charges. The dipole moment relies on the origin choice and orientation of molecule for charged systems. The lowest value of dipole moment was seen in DFT calculations for (B3LYP/ Basis Set-2) and the maximum dipole moment was seen in B3LYP/ (Basis Set-1). The same variations are seen in analysis of zero-point energies for the molecule. It is analyzed that the basis set HF/ (Basis Set-1) obtained the highest zero-point/ ground state energy among all these Slater Type Orbitals (STO) methods. be seen that value of the partition function increases with increase in Temperature, T as inferred from Fig 5. We noticed a gradual increase in q with an increase in T for low-temperature range from 50 K to 350 K. However, observed a steeper increase in q with an increase in T for high-temp range from 400 to 700 K. The increase of thermodynamical functions with temperature can also be predicted from the correlation graphics in Fig 5. The correlation equation between heat capacities, entropies, and E (thermal) using a polynomial function were curve fitted and calculated the fitting factors (R2) for them.

Table 3. Thermodynamic properties of Nitromethane using STO different basis sets

PARAMETERS	B3LYP			HF
	Basis Set-2	**Basis Set-3**	**Basis Set-1**	**Basis Set-1**
SCF energy (a.u)	–243.6247	–245.0817	–245.0917	–243.7361
Zero-point energy (kcal mol^{-1})	30.370	31.200	31.142	33.821
Rotational constants (GHz)	11.2138	12.3129	12.3278	13.0280
	10.248	10.512	10.474	10.830
	5.545	5.881	5.873	6.141
Specific heat (Cv) (cal mol^{-1} K^{-1})	13.264	12.536	12.551	11.650
Entropy (S)(cal mol^{-1} K^{-1})	70.314	69.399	69.798	68.969
Dipole moment (Debye)	3.489056	3.517475	3.801672	4.210169

Table 4. Thermodynamic functions as a function of Temp, T

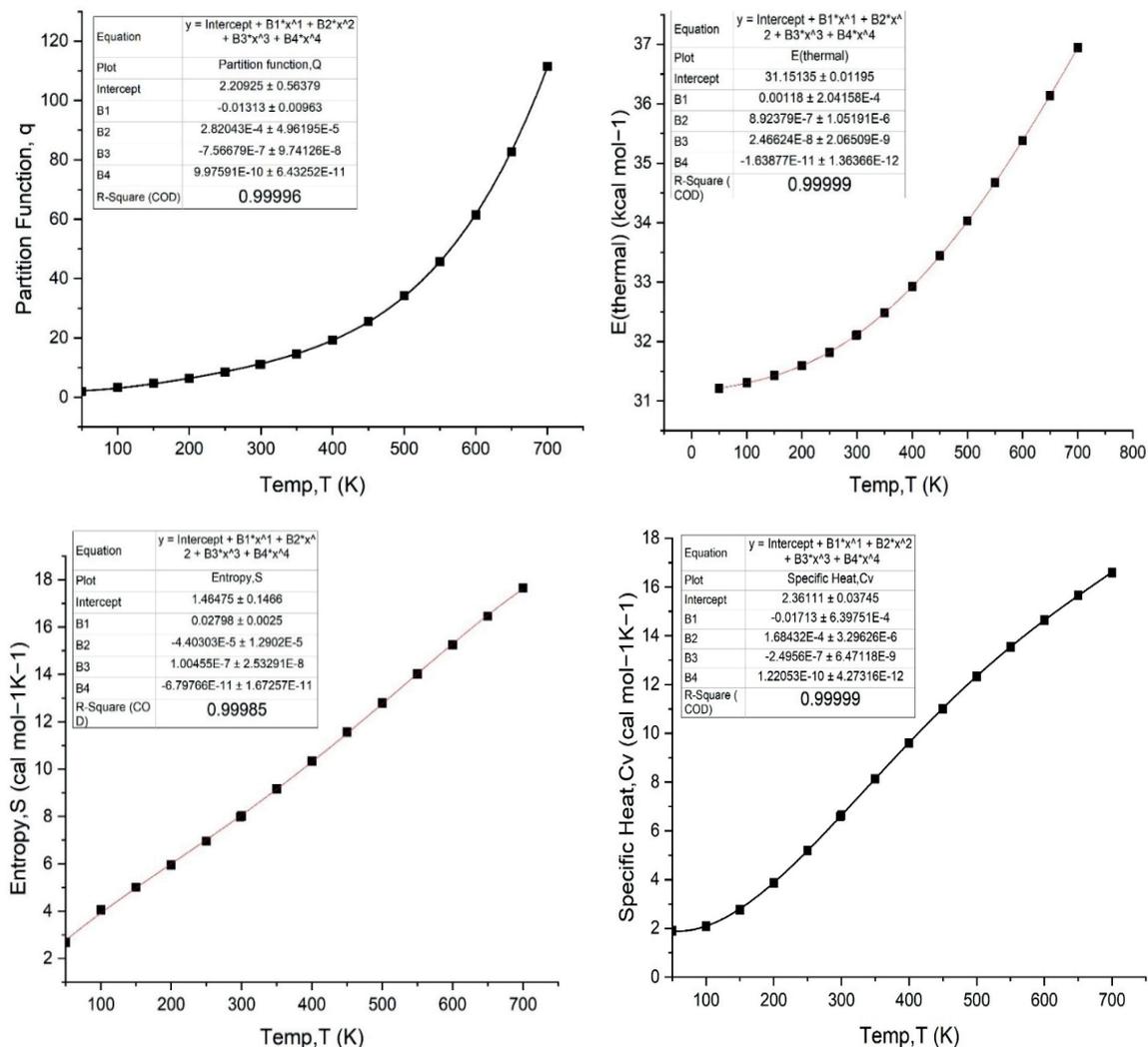| Temp, T (K)	E(thermal) (Kcal mol^{-1})	Specific heat, C_v (Cal Mol^{-1}K^{-1})	Entropy, S (Cal Mol^{-1}K^{-1})	Partition function q
50	31.210	1.904	2.686	1.9508
100	31.309	2.096	4.051	3.3166
150	31.428	2.77	5.009	4.7618
200	31.593	3.873	5.950	6.4194
250	31.819	5.199	6.954	8.4693
298.15	32.103	6.589	7.987	11.0026
300	32.115	6.644	8.028	11.1139
350	32.485	8.134	9.164	14.6116
400	32.928	9.605	10.346	19.2930
450	33.444	11.010	11.560	25.6231
500	34.028	12.324	12.789	34.1741
550	34.674	13.536	14.021	45.7717
600	35.379	14.647	15.247	61.4806
650	36.138	15.663	16.461	82.7578
700	36.944	16.594	17.656	111.4640

Figure 5. The variation of Partition function (q), E(thermal), Entropy (S), Specific Heat (Cv), as a function of temperature T

4.5. Vibrational Spectral Analysis

Vibrational spectroscopical analysis, the quantum chemical calculations are performed using different basis sets namely, B3LYP/(Basis Set-1) and HF/(Basis Set-1) for frequency analysis. We have shown here that addition of scaling factor in the B3LYP/ (Basis set-1) shows a good agreement with the available experimental values [23] which is also listed in Table 5. For comparison purposes, the simulation spectra for related Infrared and Raman range are shown in Fig 6 and 7 where the correlation of intensities and harmonic vibration wavenumbers are obtained. The molecules contain 7 atoms have Cs point group symmetry. It is already reported that the potentially active observable fundamentals of a non-linear molecule with N atoms can have a maximum value of (3N-6) [30]. So, for this molecule, we have 15 normal modes of vibration. Observed scaled vibrational frequencies using B3LYP and HF are compared with the experimental data based on normal modes analysis from the literature [23-24] with vibrational assignments are shown in Table 5.
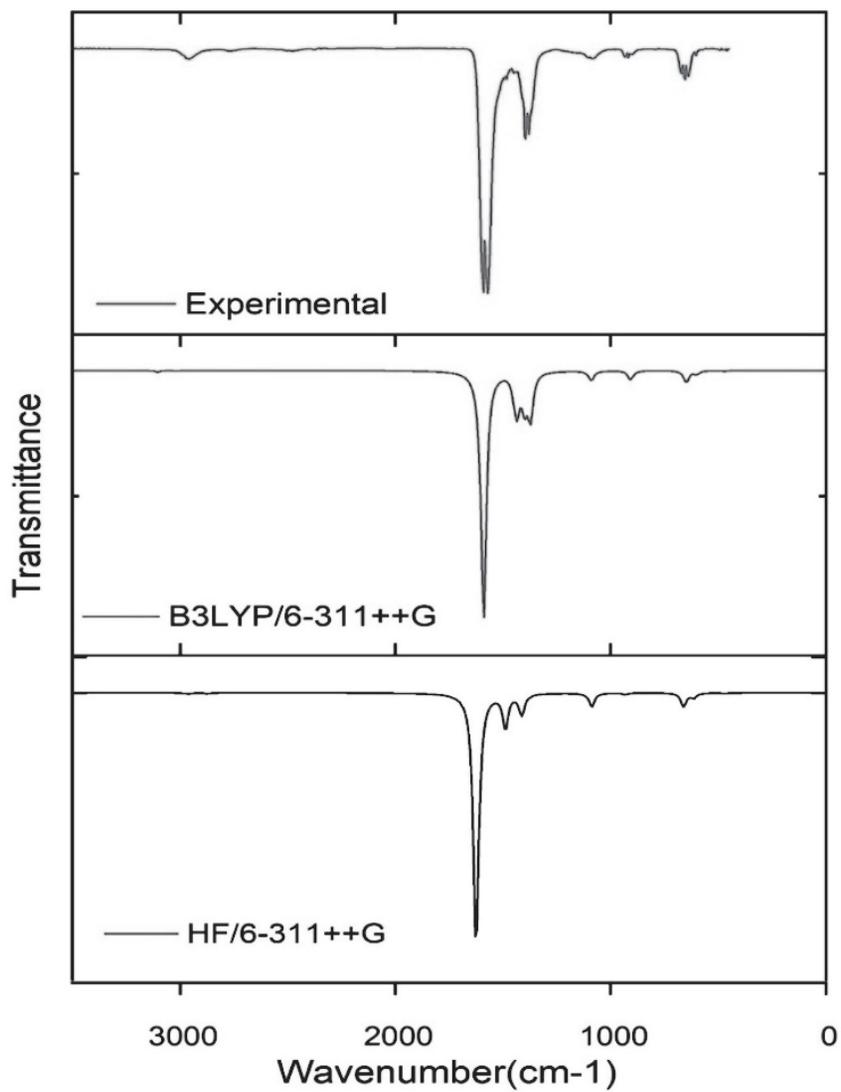
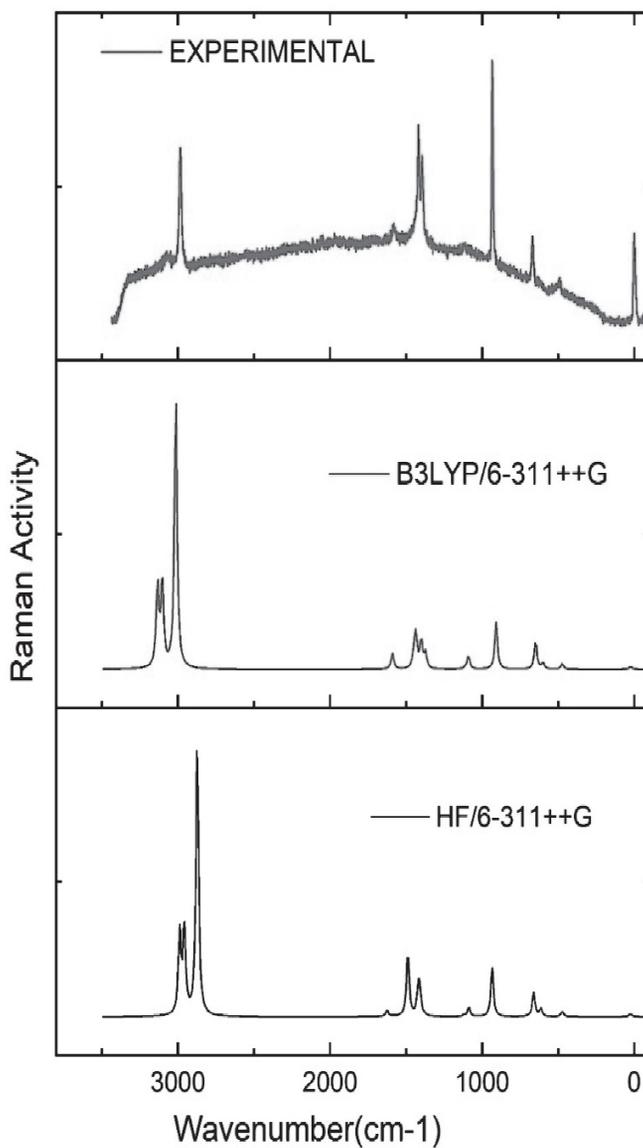**Figure 6.** Theoretical IR spectrum (after scaling) compared with Experimental [23] spectrum of Nitromethane

Figure 7. Theoretical Raman spectrum (after scaling) compared with Experimental details of Nitromethane

Table 5. Detailed assignments of vibrational wavenumber of Nitromethane

Modes	B3LYP Basis Set-1		HF Basis Set-1		Experimental				Assignments
	Un-scaled freq	Scaled freq	Unscaled freq	Scaled Freq	FT-IR [a]	Infrared gas [b]	infrared liquid [c]	FT-Raman	
ν1	25	24	28.28	25			60		$\tau(CH_3)$
ν2	483	473	531	472	494	477m	480	489	$\rho(NO_2)$
ν3	612	600	690	614	606	605m	607		$\rho(NO_2)$
ν4	662	649	743	661	654	656s	657	670	$\delta_s(NO_2)$
ν5	926	907	1049	934	918	917m	918	933	$v_s(CN)$
ν6	1111	1089	1221	1087	1082	1091m	1104		$\rho(CH_3)$
ν7	1134	1111	1258	1119	1110	1146w	1125	1111	$\rho(CH_3)$
ν8	1400	1372	14548	1378	1378	1379v.s	1379	1394	$v_s(NO_2)$
ν9	1428	1400	1585	1410	1394	1397v.s	1402		$\delta_s(CH_3)$
ν10	1464	1435	1596	1420	1450	1438m	1426	1417	$\delta_a(CH_3)$
ν11	1476	1446	1672	1488	1482		1426		$\delta_a(CH_3)$
ν12	1622	1590	1825	1624	1590	1583v.s	1560	1579	$v_a(NO_2)$
ν13	3076	2962	3229	2970	2958		2968	2984	$v_s(CH_3)$
ν14	3167	3050	3326	3058		2964m.w	3050	2987	$v_a(CH_3)$
ν15	3199	3080	3359	3090		3080v.w	3050	3073	$v_a(CH_3)$

v.s – very strong, s – strong, m – medium, m.w – medium-weak, w – weak, ν – stretching,
δ – in-plane bending, ϱ – out of plane bending,

[a]Results from Reference [23]
[b-c]Experimental dataset for nitromethane from Reference [24-25]

4.5.1. C-H vibrations

C-H stretching vibrations are observed generally with low intensity for explosive molecules that contain nitro group in the range 2900-3100 cm-1. The FT-IR frequency modes were reported at 3050 and 2968 cm-1 [23]. In this work, three hydrogen atoms are connected to a carbon atom produces three C-H stretching modes. The calculated frequencies appeared in the range 3080, 3050, 2968 cm-1 by B3LYP method, 3090, 3058, 2970 by HF method. The calculated wavenumber was found to be in the expected region with all bands having weak intensities.

C-H in-plane bending vibrations were obtained in the range 1500-1390 cm-1. The FT-IR frequency modes were obtained at 1482, 1450, 1394 cm-1 [23]. The theoretically calculated wavenumbers using HF method are obtained at 1488, 1420, 1410 cm-1, and using B3LYP method were obtained at 1446, 1435, 1400 cm-1.

C-H out of the plane bending vibrations were obtained in the range 1150 -1100 cm-1. The FT-IR frequency modes were obtained at 1110, 1082 cm-1 [23]. The theoretically calculated wavenumbers using HF method are obtained at 1119, 1087 cm-1and using B3LYP method were obtained at 1111, 1089 cm-1. The results from B3LYP/ (Basis Set-1) shows the closest values with experimental data available from the literature.

4.5.2. NO2 Vibrations

Due to the asymmetric and symmetric stretching vibrations of the NO2 group, the frequencies of NO2 molecules show strong absorptions at 1485–1570 and 1320–1370 cm-1 [32]. We report that they were observed at 1590 cm-1 and 1378 cm-1 for FT-IR and have very high intensity for asymmetry than symmetry stretching vibrations as expected. Using theoretical wavenumbers for HF method obtained at 1624, 1378 cm-1 and at 1590 and 1372 cm-1 by B3LYP method. It can be seen that the contribution to several normal modes in the low-frequency region owes to the deformation vibration of NO2 group (rocking, twisting, and scissoring) [32]. The Bands formed in these regions are also obtained and listed in Table 5.

4.5.3. C-N Vibrations

The C-N stretching frequencies are a difficult job meanwhile it faces problems in classifying these frequencies from other vibrations [31]. In this present work, we have only one C-N normal vibrational modes were observed in region 900-920 cm^{-1}. The FT-IR frequency normal modes were obtained at 918 cm^{-1} [23]. The theoretically calculated wavenumbers using HF method are obtained at 934 cm-1 and using B3LYP method are obtained at 907 cm^{-1}.

4.6. Uv-visible Spectrum And Homo/lumo Analysis

Time-dependent DFT calculations have been used on the above-optimized geometry using comprehensive basis set B3LYP/ (Basis Set-1) to obtain electronic transitions in Uv-Visible spectrum. The first 6 spins allowed singlet-singlet excitations were obtained in gas and other solvents namely, Chloroform ($CHCl_3$), Dimethyl Sulfoxide (DMSO:$(CH_3)_2$-SO) and universal solvent: water. The spectral bands are calculated at 179.75, 171.35, 163.137, 158.98 in its gas phase with oscillation strengths of 0.1675, 0.0001, 0.037, 000003. The major contributions in electronic transition energy (E), wavelength (λ), Oscillator strength(f) are computed for the gaseous state and other solvents which are listed in Table 6. SCRF (Self-Consistent Reaction Field) is a default standard procedure which accounts for the effect of a polarizable solvent (and sometimes, a classical macromolecular system) on the quantum mechanical system and exploits the Polarizable Continuum Model (PCM). A UV-Visible spectrum of the title molecule in the gas phase and DMSO, water, chloroform solvents using SCRF technique is computed and is shown in Fig 8.

HOMO/LUMO and dipole moment of nitromethane molecule were calculated in gas phase and considering different solvents (water, DMSO, acetonitrile, methanol, ethanol, acetone, and dichloromethane and it is recorded that changing solvent negligible effect on the reactivity and HOMO/LUMO bandgap energy. It is inferred that the active sites for NM are not changed as a result of interaction with the environment containing polar solvents [22].

Table 6. The electronic transition energy (E), wavelength (λ), Oscillation strength(f), Major contributions are calculated for gas phase and different solvent

Solvents	λmax (nm)	Energy(eV)	fosc	Major contribution
Gas	179.75	6.8977	0.1675	H-2 to L (92%)
	171.35	7.2357	0.0001	H to L (96%)
	163.14	7.6005	0.0370	H-1 to L+1 (97%)
	158.98	7.7986	0.0003	H-2 to L+1 (98%)
Chloroform	181.65	6.8253	0.2153	H-2 to L (93%)
	162.34	7.6373	0.0041	H to L+1 (97%)
	155.46	7.9752	0.0428	H-1 to L+1 (96%)
	150.87	150.87	0.0001	H-2 to L+1 (97%)
Dmso	181.09	6.8466	0.2145	H-2 to L (94%)
	159.60	7.7682	0.0070	H to L+1 (97%)
	153.11	8.0975	0.0306	H-3 to L (3%) and H-1 to L+1(94%)
	150.31	8.2483	0.1323	H-3 to L (3%) and H-1 to L+1(93%)
Water	180.56	6.8667	0.2082	H-2 to L (94%)
	159.46	7.7755	0.0072	H to L+1 (97%)
	152.98	8.1044	0.0267	H-3 to L (4%) and H-1 to L+1(93%)
	150.31	8.2485	0.1319	H-3 to L (4%) and H-1 to L+1(92%)

H- Homo (highest occupied molecular orbital)
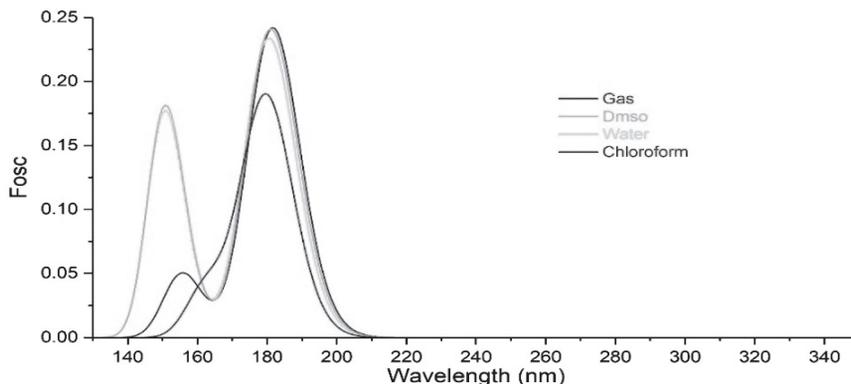L- Lumo (Lowest unoccupied molecular orbital)

Figure 8. TD-DFT UV-Visible spectrum analysis of nitromethane for gas and different solvents

CONCLUSION

The theoretical investigation and simulation of electronic structure, thermodynamic properties, and their behavior as a function of temperature, vibrational and UV-Visible spectral analysis was carried out for nitromethane molecule. The geometrical structure optimization is obtained by using DFT/B3LYP/ (Basis Set-1 (6-311++G(d,p)). Using computational methods (DFT/ HF) optimized parameters, detailed assignments of vibrational frequencies, MEP, and atomic charges were performed and plotted against experimental and scaled theoretical IR spectrum for comparison purposes and it shows an excellent agreement with the reported experimental data. The correlation of thermochemistry with temperature are also presented with a detailed plot. UV- Visible spectrum, oscillation strengths, wavenumbers, electronic energies are recorded using the Time-Dependent DFT method on optimized structure, UV-Visible spectrum determines that reported that the title molecule is also optically active.

ACKNOWLEDGEMENT

REFERENCES

Feller, D., 1996, The role of databases in support of computational chemistry calculations. J. Comput. Chem., 17: 1571-1586.

Gökhan Gece, 2008. The use of quantum chemical methods in corrosion inhibitor studies, Corrosion Science, Volume 50, Issue 11, Pages 2981-2992, ISSN 0010-938X.

Richard A. Friesner, Victor Guallar, 2005. AB INITIO QUANTUM CHEMICAL AND MIXED QUANTUM MECHANICS/MOLECULAR MECHANICS (QM/MM) METHODS FOR STUDYING ENZYMATIC CATALYSIS, Journal Article, Annual Review of Physical Chemistry, 389-427.

K. Schwarz, P. Blaha, G.K.H. Madsen, 2002. Electronic structure calculations of solids using the WIEN2k package for material sciences,Computer Physics Communications, Volume 147, Issues 1–2.

W. Kohn, A. D. Becke, and R. G. Parr, 1996. Density functional theory of electronic Structure.The Journal of Physical Chemistry.

R.G. Parr, W. Yang, 1989. Density Functional Theory of Atoms and Molecules, Oxford, New York.

Israa Zeid, Nayla El-Kork, Mahmoud Korek, 2019. Electronic structure with the calculation of the rovibrational, and dipole moments of the electronic states of the NaBr and KBr molecules, Chemical Physics, Volume 517.

Mustafa Kurt, T. Raci Sertbakan, Mustafa Özduran, Mehmet Karabacak, 2019. Infrared and Raman spectrum, molecular structure and theoretical calculation of 3,4 dichlorophenylboronic acid,Journal of Molecular Structure, Volume 921, Issues 1–3.

V. Krishnakumar, N. Prabavathi, S. Muthunatesan, 2008. Structure and vibrational frequencies of 1-naphthaldehyde based on density functional theory calculations, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Volume 69, Issue 2.

W. Chmaisani, N. El-Kork, M. Korek, 2017. Theoretical electronic structure of the NaBe molecule, Chem. Phys. 491 (33–41).

Compton, R.N., Carman, H.S. Jr., Desfrancois, C., Abdoul-Carmine, H., Schermann, J.P., Hendricks, J.H., Lyapustina, S.A., & Bowen, K.H., 1996. On the binding of electrons to nitromethane: Dipole and valence bound anions. Journal of Chemical Physics, 105(9), 3472-3478

A. W. Campbell, W. C. Davis, J. R. Travis, 1961. Shock Initiation of Detonation in Liquid Explosives, Journal Article, The Physics of Fluids,498-510.

W. D. Taylor, T. D. Allston, M. J. Moscato, G. B. Fazekas, R. Kozlowski, G. Takacs, 1980. Int. J. Chem. Kinetics 12, 231.

WEATHERBY JH, 1955. Observations on the toxicity of nitromethane. AMA Arch Ind Health. Feb;11(2):102-6. PMID: 13227634.

Krishna Prasad Shrestha, Nicolas Vin, Olivier Herbinet, Lars Seidel, Frédérique Battin-Leclerc, et al., 2020. Insights into nitromethane combustion from detailed kinetic modeling – Pyrolysis experiments in jet-stirred and flow reactors. Fuel, Elsevier, 261, pp.116349. ff10.1016/j.fuel.2019.116349ff. ffhal-02320515

Kelzenberg S, Eisenreich N, Eckl W, Weiser V, 1999. Modelling nitromethane combustion propellants. Explos Pyrotech ; 24:189–94.

Dubikhin, V.V., Nazin, G.M. & Manelis, G.B., 1999. Thermal decomposition of nitromethane. Russ Chem Bull 20, 1247–1249.

Zhang, Y.-X. and Bauer, S.H., 1999. Gas-phase decomposition mechanisms of C-NO2, N-NO2 energetic materials: Reevaluations. Int. J. Chem. Kinet.

H.Wincel, 2003. Gas-phase solvation of Cl−, NO2−, CH2NO2−, CH3NO2− and CH3NO4− by CH3NO2, International Journal of Mass Spectrometry.

Chen, E. C. M., Welk, N., Chen, E. S., & Wentworth, W. E., 1999. Electron Affinity, Gas-Phase Acidity, Bond Dissociation Energy, and Negative Ion States of Nitromethane. The Journal of Physical Chemistry.

Yinon, J., 1999. Forensic and Environmental Detection of Explosives; John Wiley & Sons: Chichester, UK.

Hend A. Ezzat; Hanan Elhaes; Ahmed Refaat; Mohamed S. Abdel-Aal; Medhat A. Ibrahim, 2021. Molecular Modeling Analyses and Vibrational Characteristics for Nitromethane, Egyptian Journal of Chemistry.

Lias, S. G., Bartmess, J. E., Liebman, J. F., Holmes, J. L., Levin, R. D., & Mallard, W. G. (2018). Ion Energetics Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69. National Institute of Standards and Technology, Gaithersburg MD, 20899.

Jones, W. J., and N. Sheppard, 1968. "The Gas-Phase Infrared Spectra of Nitromethane and Methyl Boron Difluoride; Fine Structure Caused by Internal Rotation." Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, vol. 304, no. 1477.

Deàk, J.C., Iwaki, L.K., Rhea, S.T. and Dlott, D.D., 2000. Ultrafast infrared–Raman studies of vibrational energy redistribution in polyatomic liquids. J. Raman Spectrosc., 31: 263-274.
https://doi.org/10.1002/(SICI)1097-4555(200004)31:4<263::AID-JRS538>3.0.CO;2-Q

M.J. Frisch et al., 2009. GAUSSIAN 09, Revision A.1, Gaussian, Inc., Wallingford, CT.

Megyes, Tünde & Bálint, Szabolcs & Grósz, Tamás & Radnai, Tamás & Bakó, Imre & Almásy, László, 2007. Structure of Liquid Nitromethane: Comparison of Simulation and Diffraction Studies. The Journal of chemical physics. 126. 164507. 10.1063/1.2721559.

Johnson III, R. D. NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101 Release 21 (August 2020).

Jia, C.-S., Wang, C.-W., Zhang, L.-H., Peng, X.-L., Tang, H.-M., Liu, J.-Y., … Zeng, R., 2018. Predictions of entropy for diatomic molecules and gaseous substances. Chemical Physics Letters, 692, 57–60. doi:10.1016/j.cplett.2017.12.013

G. Socrates, 2001. Infrared, Raman Characteristic Group Frequencies – Tables and Charts, 3rd ed., Wiley, New York.

K.C. Medhi, R. Barman, M.K. Sharma, 1994. Indian J. Phys. 68B 189.

P.S. Peek, D.P., 1988. Mcdermoot, Spectrochim. Acta 44 371–377.