International Journal of Physics and Applications 2025; 7(2): 205-209

International Journal
of Physics and Applications

E-ISSN: 2664-7583
P-ISSN: 2664-7575
Impact Factor (RJIF): 8.12
IJOS 2025; 7(2): 205-209
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www.physicsjournal.in
Received: 10-08-2025
Accepted: 12-09-2025

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Spectroscopic and Thermal Properties Study of Hydrogen Cyanide (HCN) Molecule Using Semi-Empirical Quantum Programs

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DOI: https://doi.org/10.33545/26647575.2025.v7.i2c.194

Abstract

In this research, the potential energy and vibrational frequencies of the linear hydrogen cyanide (HCN) molecule were studied and calculated using semi-empirical quantum programs via the MNDO-PM3 method. The geometric structure of the studied molecule was determined through initial and final matrices containing bond lengths, bond angles, and the atomic charges of each atom in the molecule. The potential energy curve of the molecule was plotted by varying the bond lengths of (H-C) and (C≡N), and corresponding total energy values were obtained. From this, the total energy was calculated as (-302.902 eV) and (-301.52 eV) for each bond respectively, along with the equilibrium bond distances of (1.09 Å) and (1.158 Å).

Also, the values of the molecular orbital energies were computed, the highest occupied molecular orbital (E_{HOMO}), the lowest unoccupied molecular orbital (E_{LUMO}), and the energy gap (Egap), the latter being found to be 14.03 eV. The vibrational frequencies had also been obtained at the equilibrium geometry. Further, thermal characteristics were calculated at varying temperatures between 100 0 K and 300 0 K and plots of each characteristic versus temperature were drawn. The findings are in good agreement with a number of prior experimental studies.

Keywords: Dissociation energy, equilibrium distance, energy gap

Introduction

The hydrogen cyanide (HCN) is commonly described as simple and at the same time, chemically powerful molecular species due to its carbon-nitrogen triple bond that provides it with a high amount of thermodynamic stability and specific electronic properties. The compound has drawn a significant academic curiosity in the fields of chemistry and physics to a great extent due to its omnipresence in experimental research labs.

The spectral study of (HCN) is of two great importance, since rotational, vibrational and electronic spectra of the molecule are used to interpret the structural conformation and charge distribution of the molecule. On the thermal properties, they define the temperature dependent behavior of the molecule, which includes the heat capacity, entropy, enthalpy, and thermal energy and are key parameters to understand the kinetics and thermodynamics of the chemical reactions involving (HCN).

On the other hand, the energy of dissociation between the atoms of the HCN molecule forms an essential characteristic of the chemical stability and reactivity of the chemical bond. This energy is also associated with the strengths of the H—C and C≡N equivalent connections and provides accurate information about the processes of chemical responses and their dynamics. [1-3].

Theory

The number of accessible energy levels in any molecular system is very big and requires some simplifications in view of elucidation. In most situations it is appropriate to treat the molecule as being a collection of different energy reservoirs. This means that the total amount of energy has to be distributed between the single reservoirs.

$$E_{total}=E_{N.O}+E_{trans}+E_{Rot}+E_{elec}+E_{vib} \qquad (1)$$

Where $E_{N.O}$ represents nuclear orientation energy, E_{trans} represents translational motion energy, ERot represents rotational energy, E_{elec} electronic energy, and E_{vib} represents vibrational energy. Our main focus is the search for vibrational energy, which represents potential and kinetic energy possessed by the molecules due to their motion, as this energy is quantized.

The vibration of the molecule is under the influence of the bond in terms of contraction and extension, which closely resembles the behavior of a spring subject to Hooke's law, hence this model is called the Simple Harmonic Oscillator (SHO). This model is considered an approximate model and can be illustrated through the relationship between potential energy and interatomic distance according to the following relationship [6].

$$V(r)=\frac{1}{2}k(r-r_e)^2 \qquad (2)$$

Where k is the force constant, V(r) the potential, r the displacement, and r_e the equilibrium distance.

The value of the potential energy reaches a minimum when the value of r equals r_e, and becomes large and positive as r deviates from r_e.

To study the vibrational spectra of molecules, an anharmonic oscillator function must be introduced. Many functions have been proposed that fit the experimental curve, the most famous of which is the Morse Potential Function [7, 9].

$$V_m=D_e(1-e^{-\beta(r-re)})^2 \qquad (3)$$

β: a constant for each electronic state of the molecule, De: represents the molecular dissociation energy.

When substituting the potential energy with the Morse function (3) in the Schrödinger equation, the vibrational energy levels are equal to (3,4):

$$E_{vib}=(v+\frac{1}{2})hv_e-(v+\frac{1}{2})hv_ex_e \qquad (4)$$

Where v_e represents the vibrational frequency in harmonic motion, v_ex_e the anharmonic constant, and v = 0,1,2…

We notice that the energy levels get closer to each other as the value of v increases. These levels can be observed as in Figure (1).

When equation (4) is written in units of wavenumbers (cm^{-1}), the term for anharmonic vibrational energy levels G(v) becomes equal to (5). [8, 10].

$$G(v)=w_e(v+\frac{1}{2})-x_ew_e(v+\frac{1}{2}) \qquad (5)$$

Figure (1) shows the experimental potential energy curve with vibrational energy levels [5].

As for thermodynamic principles, which concern the transformations of energy in matter in space depending on its state, and the resulting change in the level of internal energy (a type of potential energy in the system), it plays a role in many concepts such as:

Heat capacity, with the unit $cal·mol^{-1}·deg^{-1}$, and the relation between the heat transferred to a substance and its temperature is written as:

$$dQ=nCdT \qquad (6)$$

Where dQ is the amount of heat, n the number of moles, C the heat capacity, and dT the change in temperature.

It is known that the heat capacity can also be written as:

$$R=C_P-C_V \qquad (7)$$

Where R is the universal gas constant, C_p the heat capacity at constant pressure, and C_v the heat capacity at constant volume. The heat capacity at constant pressure for nonlinear polyatomic molecules:

$$C_P=(3/2)R+(3N-5) \qquad (8)$$

Also, enthalpy (thermal content) is an important function given by the following relationship:

$$H=U-Pv \qquad (9)$$

Where H is enthalpy, U internal energy, P pressure, and V volume.

Enthalpy is a function of pressure and temperature and energy for all substances, except for gases that behave ideally or nearly so. The differential form of enthalpy can also be explained.

$$dH=du+Pdv+vdpd \qquad (10)$$

As for heat of formation, it is a characteristic related to the stability of the compound. If it is large and positive, the compound is unstable; if it is negative, the compound is stable. That is, when most heats of formation are negative, it means the formation of the compound from its elemental components is usually exothermic (q or T), and in this case, the compound is more stable because its thermal content is lower than the sum of the thermal contents of the elements forming it.

Another function is entropy (S), which is considered a measure of the randomness of the compound resulting from temperature changes, and is given by the following relation.

$$ds=dqr/T \qquad (11)$$

The importance of the research lies in the development and determination of the required thermal range in industrial materials in a better way, relying on a set of studies and sources conducted within a modern applied scope [11].

Results and Calculations

1. Hydrogen Cyanide Molecule (HCN)

The structural diagram of the hydrogen cyanide molecule HCN was drawn using the program Hyperchem8.0, which is based on internal coordinates (r, ɵ, φ), where r is the bond length in angstroms, ɵ represents the angles between three atoms and is measured in degrees, and φ represents the dihedral angles and is also measured in degrees.

Figure No. (2) represents the geometric structure at the equilibrium state. After drawing the molecule and obtaining the best geometric configuration (Optimization), we obtain the initial matrix of the molecule as in Table No. (1), which contains the atoms composing the molecule, the distances between atoms (bond lengths), the best positioning of these atoms (Opt), the angles between the bonds, and the dihedral angles.

After obtaining the initial matrix and inputting it into the program WinMopac7.21, we are able to obtain some important properties: the total energy, the final heat of formation, electronic energy, bonding energy, and repulsion energy, as shown in Table No. (2).

Table 1: Initial matrix of the hydrogen cyanide molecule HCN

Atom	r A°	Opt	ɵ	Opt	φ	Opt	ABC
H	0000.0000	0	00000.0000	0	0000.0000	0	000
C	0001.0702	1	00000.0000	0	0000.0000	0	100
N	0001.1556	1	00179.9999	1	0000.0000	0	210

Table 2: Some important results for the HCN molecule calculated using the program HyperChem8.0

Quantity	Value	Unit
Heat of formation	33.08951	Kcal/mol
Total Energy	-6804.1904	Kcal/mol
Total energy	-10.84316	a.u
Binding Energy	-302.9024	Kcal/mol
Core-Core interaction	5839.421	Kcal/mol
Electronic Energy	-12643.612	Kcal/mol
Isolated Atomic energy	-6501.2879	Kcal/mol

2. Anharmonic Potential Energy Curve for HCN Molecule

The potential curve proved the stability state at a certain distance between the atoms (H—C) and (C≡N), where we obtain the total energy values from changing the bond lengths between the atoms mentioned above. We draw the potential energy curve for the HCN molecule, and when the atoms are brought closer to each other, a repulsive force arises accompanied by high potential energy that increases rapidly, and the attractive force is weak accompanied by low potential energy that increases less rapidly when the atoms are moved further apart than the equilibrium distance. We continue to increase the distance until the bond breaks, and the energy becomes a straight line, and the curve deviates from harmonic behavior to anharmonic behavior. From it, the dissociation energy is calculated as shown in Figures (3) and (4).

3. Calculation of Vibrational Frequencies of HCN Molecule

After drawing the potential curve for the HCN molecule through the program Hyperchem8.0, the vibrational frequencies were calculated in units (cm^{-1}), the intensity in units (km/mol), and the symmetry for each frequency as shown in Table (3).

The vibrational frequencies for the HCN molecule are confined between (932.41, 3146.93 cm^{-1}), and the highest intensity was (51.11232 km/mol) at the frequency (3146.93 cm^{-1}).

Table 3: Values of vibrational frequencies, intensity, and symmetry for the hydrogen cyanide molecule HCN calculated using the programs HyperChem8.0 and WinMopac7.21

Vibration Mode	Hyper Chem8.0			WinMopac7.21
	Intensity	wave number	Symmetry	Wave number
1	21.89324	932.41	1 PI	855.99
2	21.89328	932.43	1PI	856.14
3	16.39370	2267.24	1SI	2286.28
4	51.11232	3146.93	2SI	3297.72

4. Molecular Orbital Energy Eigenvalues of HCN Molecule

The molecular orbitals and the energy values for each orbital and the symmetry of each molecular level were obtained through the aforementioned programs, where the number of orbitals occupied by electrons was (4), and the unoccupied ones were (3). The energy of the highest occupied molecular orbital, denoted as E_{HOMO}, and the energy of the lowest unoccupied molecular orbital, denoted as E_{LUMO}, were calculated by calculating the energy values of the molecular orbitals measured in units (eV), and the energy gap (Egap) was calculated using the following relation:

$E_{gap} = E_{LUMO} - E_{HOMO}$The energy gap was (14.02 eV) for the molecule, as shown in Figure (5).

5. Thermal Properties of the Hydrogen Cyanide Molecule

Among the most important properties calculated are the thermal properties, which determine the most important conditions based on which reactions occur between molecules, where the heat of formation was calculated as in Figure (6), as well as the thermal content (enthalpy) as in Figure (7), and in the same way the heat capacity was calculated as in Figure (8), and the entropy as in Figure (9), for the hydrogen cyanide molecule HCN at the equilibrium state through the program WinMopac7.21 after obtaining the final matrix through the program HyperChem8.0.

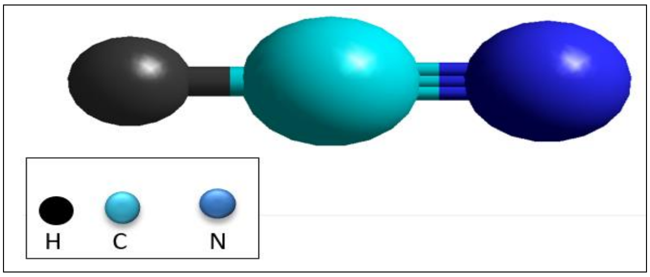

Fig 1: Geometric structure of the hydrogen cyanide molecule HCN drawn in HyperChem8.0

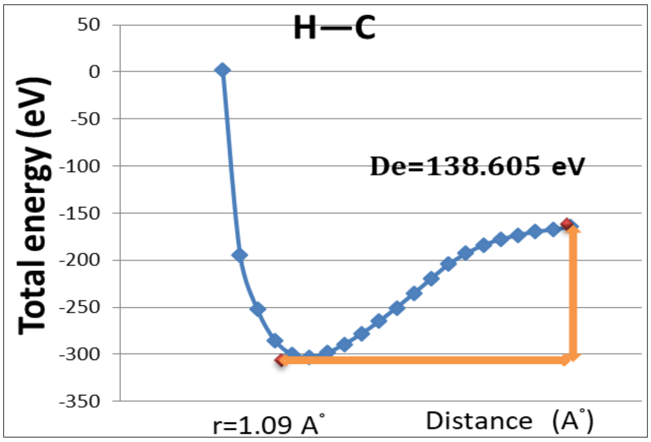

Fig 2: The relationship between potential energy and bond length between two atoms (H−C) for the HCN molecule using the program WinMopac7.21

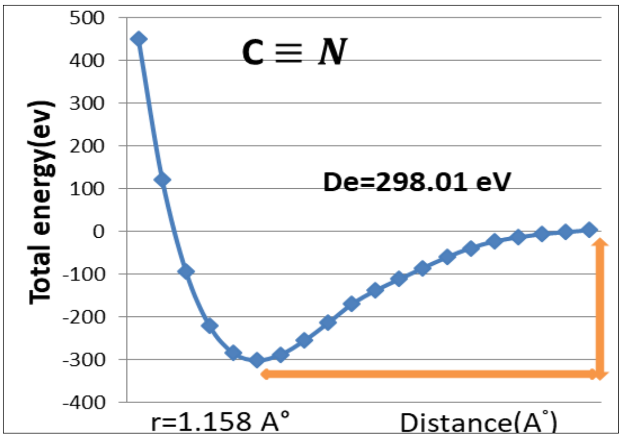

Fig 3: The relationship between potential energy and bond length between two atoms (C≡N) for the HCN molecule using the program WinMopac7.21

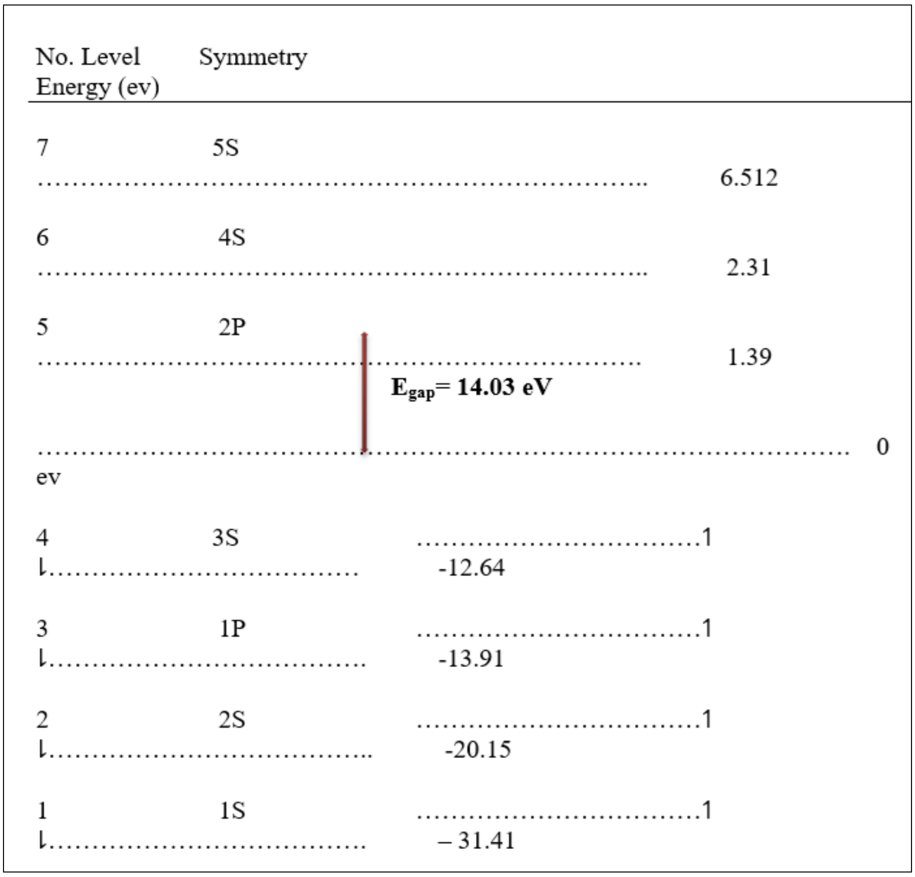

Fig 4: Energy levels of the hydrogen cyanide molecule HCN showing the highest occupied molecular orbital (HOMO), the lowest unoccupied orbital (LUMO), and the symmetry of each orbital

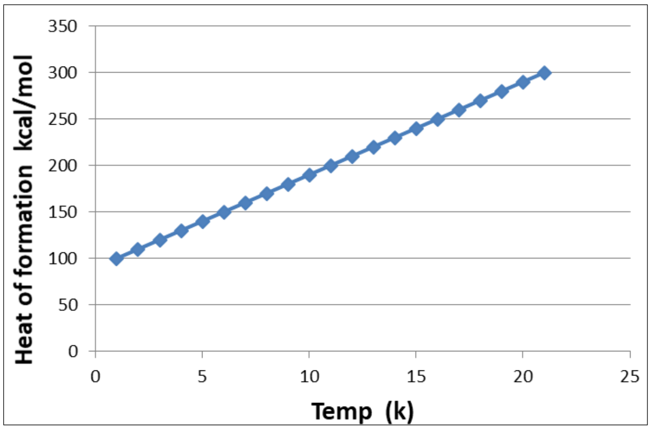

Fig 5: Shows the relationship between heat of formation (H.O.F) and temperature (T) for the HCN molecule

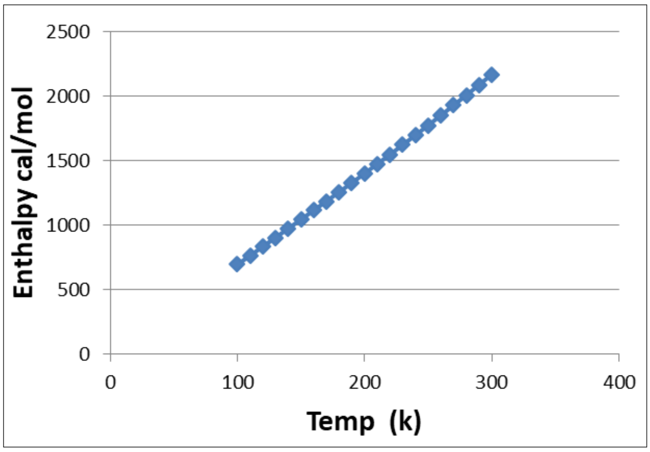

Fig 6: The relationship between enthalpy (H) and temperature (T) for the HCN molecule

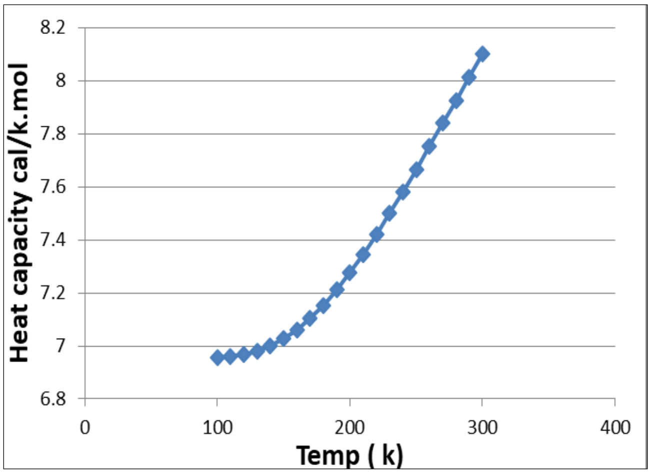

Fig 7: The relationship between heat capacity (CP) and temperature (T) for the HCN molecule

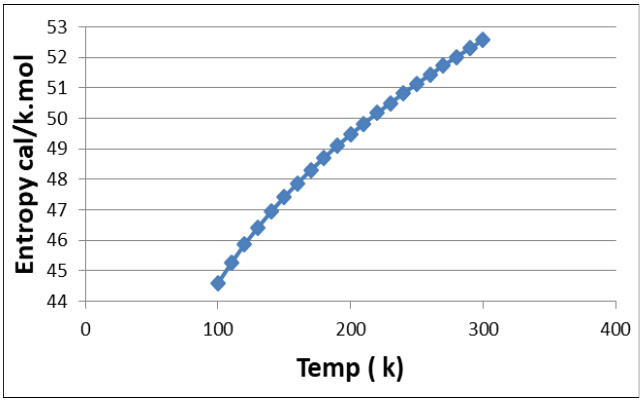

Fig 8: The relationship between entropy (S) and temperature (T) for the HCN molecule

Conclusion

The spectral properties of the hydrogen cyanide molecule HCN, which contains the bonds (H−C) and (C≡N), were studied and calculated using the semi-empirical method MNDO-PM3 and some spectral properties were obtained.

This study was carried out at the stable form of the molecule at the lowest total energy and at the equilibrium distance ($r = r_e$), and it was found that:

1. The total bond energy for (H−C) is (−302.38 eV), and the total bond energy for (C≡N) is (−301.52 eV).
2. The bond (C≡N) in the HCN molecule is more stable compared to the C—H bond due to its triple nature, high strength, and large bond energy.
3. The (H−C) bond has a dissociation energy of (268.76 eV), and the (C≡N) bond has a dissociation energy of (298.01 eV), where the (H—C) bond is weaker and less stable and thus breaks first during chemical reactions because it requires less energy for dissociation.
4. The stretching of the (H−C) bond has high frequencies because the masses of the vibrating atoms are very small, where the frequency is inversely proportional to the mass according to the relation:

$$V=1/2\pi\sqrt{\frac{K}{\mu}}$$

Where k is the bond force constant, and μ is the reduced mass

5. The hydrogen cyanide molecule HCN has four occupied molecular orbitals HOMO, and the value of the highest occupied orbital is (−12.6 eV), and the number of unoccupied orbitals is three, with the lowest LUMO value being (1.39 eV), and the energy gap is (14.02 eV), calculated from the relation:

$$Egap = E_{LUMO} - E_{HOMO}$$

Therefore, the energy gap represents a measure of the chemical stability of the molecule. In HCN, the gap is moderate, so the molecule is relatively stable but has reactivity at the sites of the triple bonds.

6. The IR spectrum of the studied molecule can be analyzed into regions specific to vibrational frequencies, as the molecule shows a small number of vibrational frequencies due to the 3N−5 rule, where it contains four vibrations: stretching vibration (changing the bond length between two atoms), and bending vibration (changing the angles between two atoms connected to a central atom without significant change in bond length).
7. We note that the thermal properties (entropy, enthalpy, and heat content) increase as the complexity of the molecule increases, and this can be explained according to quantum mechanics, as the increase in molecular complexity requires high energy and high temperatures to induce changes in thermal properties.

At low temperatures, translational and rotational motion contribute to heat capacity, and at high temperatures, vibrational motion is taken into account. Therefore, vibrational energy does not affect heat capacity at low temperatures.

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