

RESEARCH ARTICLE

Spectroscopic Estimation of Thermodynamic Properties of Copper Monohalides (CuF, CuCl, CuBr, and CuI)

Shipra Tripathi¹, Anjani K. Pandey^{2,*}, Kailash Narayan Uttam³, C. K. Dixit⁴

ABSTRACT: This paper presents a detailed investigation into the thermodynamic properties of copper monohalides (CuF, CuCl, CuBr, and CuI) based on spectroscopic data and partition function theory. Key thermodynamic quantities, including Gibbs free energy (G), enthalpy (H), entropy (S), and specific heat capacity at constant pressure (C_p), are calculated over a broad temperature range of 100 K to 3000 K. The analysis incorporates anharmonicity, nonrigidity, and stretching effects to improve the accuracy of the results. The relationship between temperature and these thermodynamic properties is explored through different modes of molecular motion, such as rotational, vibrational, and translational. Our results offer valuable insights into the behavior of copper monohalides, contributing to their application in fields like material science, nanotechnology, and industrial processes. These data are essential for designing copper-based compounds with optimized thermodynamic properties in advanced technological applications.

Keywords: Diatomic Molecules, Partition Function, Entropy, Free energy, Molecular motion.

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1. INTRODUCTION

Copper is a versatile element that plays a significant role in various scientific and industrial applications due to its distinctive properties [1]. It is highly valued for its excellent conductivity, both electrical and thermal, as well as its ductility, which allows it to be shaped and formed into various materials and devices. Copper alloys, such as brass and bronze, have been used for centuries and continue to hold substantial industrial importance. Additionally, copper

compounds have found applications in diverse fields [2]. For instance, copper-based compounds like Fehling's solution are widely employed in analytical chemistry, particularly for testing the presence of reducing sugars. Furthermore, copper is commonly used as an algicide in water purification processes, underscoring its broad utility [3]. One of the primary reasons for the growing interest in copper in recent years is its potential in the field of nanoscience and nanotechnology. When reduced to the nanoscale, copper exhibits unique properties that differ considerably from its bulk form [4]. For example, the melting point of copper nanomaterials drops to approximately one-eighth of that of bulk copper, and it becomes transparent to visible light, a stark contrast to the opaque nature of bulk copper. These nanoscale properties make copper highly attractive for various cutting-edge applications, particularly in electronics, catalysis, and materials science. Copper is also an abundant natural element, commonly found in soil, water, and rocks. It is one of the functional metals that has greatly enhanced the quality of human life [5, 6]. In agriculture, copper is crucial for the optimal growth of plants, acting as an essential

¹ Department of Physics, Dr. R K Pal Degree College, Kannauj, Uttar Pradesh, India

² Department of Applied Science and Humanities, Institute of Engineering & Technology, Dr. Shakuntala Misra National Rehabilitation University, Lucknow, Uttar Pradesh, India

³ Saha's Spectroscopy Laboratory, Department of Physics, University of Allahabad, Prayagraj, India

⁴ Department of Physics, Faculty of Science & Technology, Dr. Shakuntala Mishra National Rehabilitation University, Lucknow, Uttar Pradesh, India

* Author to whom correspondence should be addressed:
anjani_phys@yahoo.in (Anjani K. Pandey)

nutrient required for living tissues. Copper ions serve as cofactors in several enzymatic processes, playing a critical role in plant physiology. The presence of copper in soil and water helps sustain a healthy ecosystem, further highlighting its significance [6, 7].

In recent years, copper's thermodynamic properties have gained attention, especially in the context of manufacturing smart materials and advancing automation technology. Thermodynamic data related to copper compounds, particularly copper monohalides, have been found useful in various applications, including diagnosing heart diseases and designing nanomaterials. Researchers have attempted to calculate key thermodynamic quantities of copper monohalide compounds over a wide temperature range (100-2500K) [8]. Spectroscopic data serve as reliable input for these calculations, enabling the accurate prediction of thermodynamic behavior under different conditions [9]. The calculation of thermodynamic properties involves partition function theory, which allows scientists to predict how different modes of molecular motion contribute to the overall energy of a system. For diatomic molecules like copper monohalides, four types of motion are typically considered: translational, rotational, vibrational, and electronic. These motions correspond to different forms of energy: translational energy relates to the movement of molecules through space, rotational energy involves the spinning of the molecules around their center of mass, vibrational energy arises from the periodic stretching and compressing of molecular bonds, and electronic energy refers to the movement of electrons within the molecule [10, 11].

In the calculation of thermodynamic quantities, it is essential to account for effects such as anharmonicity and nonrigidity. Anharmonicity refers to deviations from the ideal harmonic oscillator model, which assumes that molecular vibrations occur in perfect, regular intervals. In reality, molecular vibrations often deviate from this ideal behavior, especially at higher temperatures. Similarly, nonrigidity refers to the fact that molecules are not perfectly rigid and may undergo structural changes or distortions as they move. By incorporating these effects, researchers can achieve more accurate thermodynamic predictions, improving our understanding of how copper compounds behave under various temperature conditions [12].

The study of copper's thermodynamic properties not only enhances our fundamental understanding of this important element but also has practical implications. For instance, copper's unique properties at the nanoscale make it a promising candidate for the development of advanced nanotechnologies, including next-generation electronic devices and smart materials. Additionally, understanding the thermodynamic behavior of copper compounds may lead to new insights into their biological roles, potentially paving the way for innovations in agricultural science and medicine [13, 14].

In this paper, we focus on the thermodynamic properties of copper monohalide compounds over a wide temperature range (100-2500K). We calculate key thermodynamic quantities using partition function theory, incorporating

anharmonicity and nonrigidity effects for enhanced accuracy. Our analysis examines how different molecular motions—translational, rotational, vibrational, and electronic—contribute to the overall thermodynamic behavior of copper monohalides. By doing so, we aim to elucidate the temperature-dependent variation in these quantities and explore the broader implications of our findings in the fields of nanotechnology, materials science, and potential medical applications.

2. THEORY

The rotational energy of a diatomic molecule is given by equation in the non-rigid rotator model.

$$E_{rot} = [B_e J(J+1) - D_e J^2(J+1)^2] \hbar c \quad (1)$$

where, E_{rot} is the rotational energy, J is the rotational quantum number, h is Planck's constant, c is the velocity of light, B_e is the rotational constant and D_e is the centrifugal constant.

Equation provides the expression for vibrational energy in the context of the anharmonic oscillator model:

$$E_{vib} = \left[\omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \right] \hbar c \quad (2)$$

where, ω_e is the vibrational constant, $\omega_e x_e$ is the anharmonicity constant and v is the vibrational quantum number.

Thermodynamically quantities like Free Energy (F), Enthalpy (H), Entropy (S) and Heat Capacity (C) are related with partition function. Thus if partition function is known, computation of a molecular system can be performed. The partition function associated with any thermodynamic system can be presented as [14-15]:

$$Z = \sum_i g_i e^{-\frac{E_i}{kT}} \quad (3)$$

where g_i is the degeneracy of energy levels, E_i is the energy of i^{th} level, K is Boltzmann constant, T is absolute temperature and i range over all quantum states.

In case of diatomic molecules four types of energies viz. electronic, vibrational, rotational and translational contribute to the total energy [14]:

$$E_t = E_r + E_v + E_e + E_{tran} \quad (4)$$

where, E_t , E_r , E_v , E_e and E_{tran} denote total energy, rotational energy, vibrational energy, electronic energy, and translational energy, respectively.

The four types of energies give raise four types of partition functions. Thus total partition function of the system can be

written as:

$$Z = Z_{\text{tran}} \cdot Z_r \cdot Z_v \cdot Z_e \quad (5)$$

In the above expression Z_e does not play any important role as electronic energy (10 eV) is very high as compare to vibrational energy (10^{-2} eV) and rotational energy (10 eV). Therefore Z_e can be neglected and we have $Z = Z_{\text{tran}} \cdot Z_r \cdot Z_v$. Treating the diatomic molecule as the molecule of ideal gas, the translational partition function at one atmospheric pressure can be written as:

$$Z_{\text{tran}} = 0.002566M^{1.5}T^{2.5} \quad (6)$$

where, M and T denote molecular weight and temperature T in Kelvin respectively. Applying Rigid rotator model, Harmonic oscillator model and incorporating nonrigidity and anharmonicity effects, vibration-rotation partition function Z_{vr} can be simplified as [16-18]:

$$Z_{vr} = \frac{1}{\sigma y \{1 - \exp(-u)\}} \left[1 + \frac{2\beta}{y} + \frac{\delta}{\{\exp(u)-1\}} + \frac{2ux}{\{\exp(u)-1\}^2} + \frac{y}{3} + \frac{y^2}{15} \right] \quad (7)$$

Or

$$Z_{vr} = Z_I Z_C \quad (8)$$

where, Z_I represents the ideal partition function which is valid for the perfectly rigid-rotator harmonic oscillator model and Z_C represents a correction in the partition function and gives the contribution due to centrifugal stretching, nonrigidity and anharmonicity of a diatomic molecules. Thus, the total partition function becomes:

$$Z_t = \frac{1}{\sigma y \{1 - \exp(-u)\}} (0.002566M^{1.5}T^{2.5}) \left[1 + \frac{2\beta}{y} + \frac{\delta}{\{\exp(u)-1\}} + \frac{2ux}{\{\exp(u)-1\}^2} + \frac{y}{3} + \frac{y^2}{15} \right] \quad (9)$$

Using this partition function thermodynamical quantities can be calculated using following equations [19-20]:

Free energy:

$$(F - H_0)_{vr} = -RT \ln Z_{vr} - RT \ln x \quad (10)$$

Enthalpy:

$$(H - H_0)_{vr} = RT^2 \frac{\partial}{\partial T} (\ln Z_{vr}) + RT \ln x \quad (11)$$

Entropy:

$$S_{vr} = R \left[(1 + \ln Z_{vr}) \right] + RT \left[\frac{\partial}{\partial T} (\ln Z_{vr}) \right] \quad (12)$$

Heat capacity at constant pressure:

$$Cp_{vr} = RT \frac{\partial}{\partial T} (\ln Z_{vr}) \quad (13)$$

where, x represents the multiplicity of the ground state.

The translational contribution and the vibrational-rotational contribution are added to determine the thermodynamic variables such as free energy, enthalpy, entropy, and heat capacity of germanium diatomic molecular gases [21-22].

3. RESULTS AND DISCUSSION

The thermodynamic properties of copper monohalides (CuF, CuCl, CuBr, and CuI) have been systematically investigated across a wide temperature range. The key thermodynamic quantities, namely free energy (F), enthalpy (H), entropy (S), and specific heat (Cp), are presented in Table 1 and 2. These values were calculated using molecular partition functions and spectroscopic data, as provided in Table 3. Additionally, the comparison between calculated and observed thermodynamic quantities at 300 K is detailed in Table 4, showcasing a strong correlation for CuF, CuCl, and CuBr, while data for CuI is not available in the literature.

3.1. Free Energy (F)

Free energy is a crucial parameter for understanding the stability of molecules at different temperatures. As seen in Table 1 and 2, the free energy of all four copper monohalides increases with temperature. This is expected, as an increase in temperature raises the overall energy of the system, making it less energetically favorable. For instance, at 100 K, the free energy of CuF is 18.18 kJ/mole, which rises to 691.11 kJ/mole at 2500 K. Similarly, free energy of CuCl increases from 19.00 kJ/mole at 100 K to 720.80 kJ/mole at 2500 K. This trend holds true for both CuBr and CuI as well. The rising free energy values indicate that the molecules become more unstable at higher temperatures, as molecular interactions become more dynamic and disordered (Figure 1).

The comparable behavior of the free energy for CuF, CuCl, CuBr, and CuI suggests that the halide component does not significantly alter the thermodynamic stability of the copper-halogen bonds, even though the molecular weights of the compounds vary. However, the small differences in free energy between the different copper halides can be attributed to the increasing size of the halogen atoms (from F to I), which impacts the molecular interactions at higher temperatures.

3.2. Enthalpy (H)

Enthalpy represents the total heat content of a system and is closely related to the internal energy of the molecules. As shown in Table 1 and 2, the enthalpy of the copper

monohalides increases with temperature, which is consistent with the expectation that the total heat content of a system rises as temperature increases. For CuF, the enthalpy increases from 3.07 kJ/mole at 100 K to 75.70 kJ/mole at 2500 K, while for CuCl, it grows from 3.07 kJ/mole at 100 K to 76.46 kJ/mole at 2500 K. The values for CuBr and CuI follow similar trends, with higher enthalpy values corresponding to higher temperatures (Figure 2).

This increase in enthalpy is primarily due to the contributions from translational, rotational, and vibrational motions of the molecules. At lower temperatures, only the translational motion is active, contributing to lower enthalpy values. As the temperature rises, the rotational and vibrational motions are excited, leading to a corresponding increase in the enthalpy. The significant increase in enthalpy at higher temperatures indicates that the molecules absorb more energy, leading to more dynamic molecular interactions.

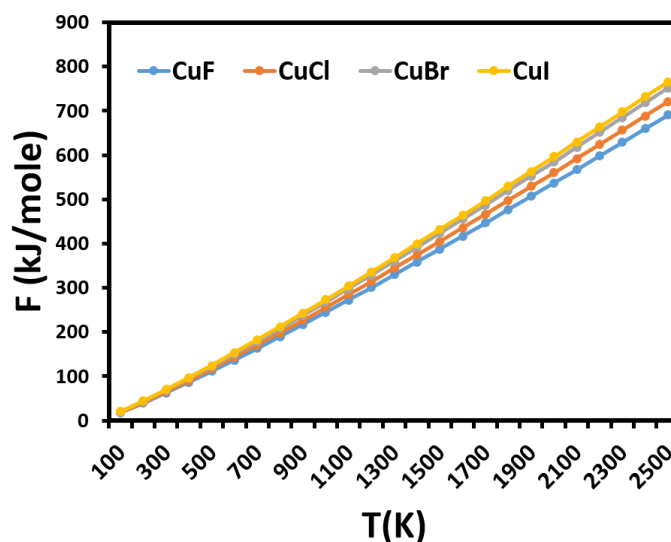


Fig. 1. Variation of Free energy (F) with temperature (T).

Table 1. Calculated thermodynamical quantities for CuF and CuCl molecules.

T(K)	CuF molecule				CuCl molecule			
	F	H	S	C _p	F	H	S	C _p
100	18.18	3.07	201.97	30.22	19.00	3.07	210.47	31.57
200	39.43	6.67	222.81	32.48	41.18	6.73	232.93	35.21
300	62.30	9.67	236.04	33.70	65.12	9.69	247.17	36.74
400	86.32	12.59	245.95	36.00	90.28	12.61	256.59	37.40
500	111.22	13.52	253.87	36.75	116.35	15.55	265.78	37.74
600	136.84	18.45	260.45	37.20	143.16	18.50	272.53	37.92
700	163.06	21.38	266.08	37.49	170.59	21.46	278.26	38.04
800	189.81	24.33	270.98	37.69	198.55	24.43	283.24	38.11
900	217.02	27.28	275.33	37.82	226.98	27.41	287.64	38.17
1000	244.63	30.25	279.24	37.92	255.82	30.39	291.59	38.20
1100	272.62	33.22	282.78	38.00	285.03	33.39	295.17	38.23
1200	300.94	36.20	286.03	38.06	314.58	36.40	298.43	38.25
1300	329.58	39.19	289.02	38.10	344.45	39.42	301.44	38.26
1400	358.50	42.19	291.79	38.14	374.60	42.45	304.23	38.27
1500	387.68	45.19	294.37	38.16	405.01	45.49	306.83	38.28
1600	417.11	48.20	296.79	38.19	435.68	48.54	309.27	38.29
1700	446.78	51.23	299.06	38.21	466.58	51.60	311.56	38.29
1800	476.66	54.26	301.21	38.22	497.70	54.67	313.72	38.30
1900	506.75	57.29	303.24	38.23	529.02	57.76	315.76	38.30
2000	537.04	60.34	305.17	38.24	560.55	60.85	317.70	38.30
2100	567.51	63.40	307.01	38.25	592.26	63.95	319.55	38.30
2200	598.16	66.46	308.76	38.26	624.14	67.06	321.31	38.30
2300	628.98	69.53	310.44	38.27	656.20	70.18	322.99	38.30
2400	659.97	72.61	312.04	38.27	688.42	73.31	324.61	38.30
2500	691.11	75.70	313.58	38.28	720.80	76.46	326.16	38.30

Where, F is free energy (kJ/mole), H is enthalpy (kJ/mole), S is entropy (J/mole/K), C_p is specific heat (J/mole/K) and T is temperature (K).

Table 2. Calculated thermodynamical quantities for CuBr and CuI molecules.

T	CuBr molecule				CuI molecule			
	F	H	S	C _p	F	H	S	C _p
100	20.01	3.07	221.49	33.22	20.46	3.07	226.06	34.27
200	43.32	6.75	246.15	36.48	44.29	6.76	250.23	37.02
300	68.46	9.69	261.61	37.46	70.00	9.70	265.02	37.73
400	94.84	12.62	272.82	37.84	96.95	12.62	275.66	38.01
500	122.15	15.56	281.58	38.03	124.84	15.57	283.96	38.14
600	150.20	18.51	288.77	38.13	153.47	18.52	290.77	38.21
700	178.88	21.47	294.85	38.19	182.73	21.48	296.53	38.25
800	208.09	24.44	300.12	38.23	212.52	24.45	301.53	38.28
900	237.77	27.42	304.76	38.26	242.78	27.44	304.95	38.29
1000	267.86	30.40	308.92	38.28	273.45	30.42	309.91	38.31
1100	298.32	33.40	312.67	38.29	304.50	31.42	313.49	38.32
1200	329.13	36.41	316.09	38.30	335.88	36.43	316.76	38.32
1300	360.24	39.43	319.23	38.31	367.58	39.45	319.77	38.33
1400	391.65	42.45	322.13	38.32	399.57	42.48	322.57	38.33
1500	423.32	45.49	324.83	38.32	431.82	43.52	325.17	38.33
1600	455.24	48.54	327.36	38.32	464.32	48.57	327.60	38.33
1700	487.39	51.59	329.72	38.32	497.06	51.63	329.89	38.33
1800	519.76	54.66	331.95	38.33	530.02	54.70	332.05	38.33
1900	552.34	57.73	334.06	38.33	563.18	57.70	334.09	38.33
2000	584.12	60.82	336.06	38.33	596.54	60.86	336.03	38.33
2100	618.09	63.91	337.95	38.33	630.09	63.96	337.88	38.33
2200	651.23	67.02	339.76	38.32	663.81	67.07	339.64	38.33
2300	684.54	70.13	341.48	38.32	697.71	70.18	341.32	38.33
2400	718.02	73.25	343.13	38.32	731.76	73.31	342.93	38.32
2500	751.65	76.39	344.71	38.32	765.98	76.45	344.48	38.32

Where, *F* is free energy (kJ/mole), *H* is enthalpy (kJ/mole), *S* is entropy (J/mole/K), *C_p* is specific heat (J/mole/K) and *T* is temperature (K).

Table 3. Spectroscopic Constants of Copper mono halides [3].

Molecule	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$	MW (a.m.u)	Ground State
CuF	622.7	3.95	0.3794029	0.0032298	82	$1\Sigma^+$
CuCl	415.29	1.58	0.1762880	0.0009964	100	$1\Sigma^+$
CuBr	314.8	0.96	0.1019262	0.0004521	142	$1\Sigma^+$
CuI	264.5	0.60	0.0732874	0.0002839	190	$1\Sigma^+$

Table 4. Comparison of Calculated and Observed Thermodynamical Quantities at 300K [3].

Molecule	S _{cal}	S _{obs}	C _{pcal}	C _{pobs}
CuF	232.93	230.3	35.21	34.9
CuCl	246.15	245.1	36.48	35.7
CuBr	250.23	251.8	37.02	36.6

Where, *S* is Entropy (J/mole/K) and *C_p* is Specific heat (J/mole/K).

The similarity in the enthalpy trends across the four copper monohalides also suggests that the copper-halide bond strength is not significantly altered by the different halogens. However, the increasing molecular weight from CuF to CuI does result in small differences in the enthalpy values, with heavier molecules like CuI showing slightly higher enthalpy at elevated temperatures.

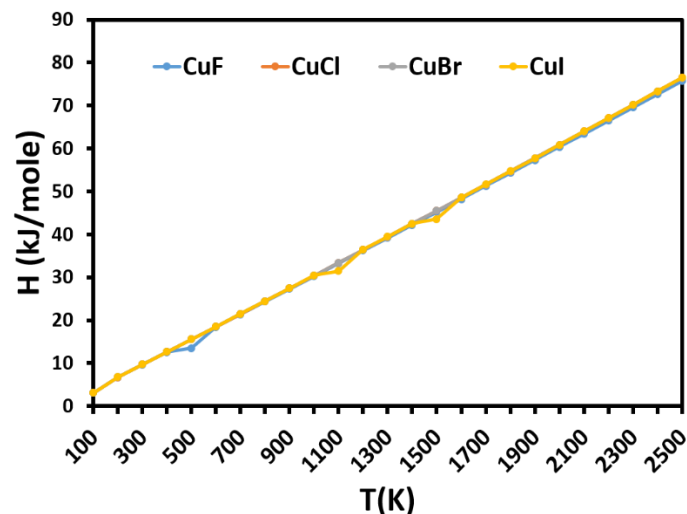


Fig. 2. Variation of enthalpy (H) with temperature (T).

3.3. Entropy (S)

Entropy measures the degree of disorder or randomness in a system, and it plays a vital role in understanding molecular motion. As seen in Table 1 and 2, the entropy of the copper monohalides increases with temperature, as expected. For CuF, the entropy increases from 201.97 J/mole/K at 100 K to 313.58 J/mole/K at 2500 K, while for CuCl, the entropy rises from 210.47 J/mole/K at 100 K to 326.16 J/mole/K at 2500 K. The values for CuBr and CuI exhibit similar trends (Figure 3). At lower temperatures, the molecular motions are limited primarily to translational motion, leading to lower entropy values. As the temperature increases, rotational and vibrational motions are excited, leading to a greater number of accessible energy states and, consequently, higher entropy. The increase in entropy reflects the growing disorder within the system as more molecular motions become energetically accessible. The similarity in the entropy values for CuF, CuCl, CuBr, and CuI indicates that the halogen atom does not significantly influence the overall disorder of the system. However, slight variations in entropy can be observed due to the increasing size of the halogen atom, with larger atoms (e.g., Iodine in CuI) contributing to slightly higher entropy values at higher temperatures.

3.4. Specific Heat Capacity (Cp)

The specific heat capacity (Cp) is an essential thermodynamic property that describes the amount of heat

required to raise the temperature of a system by one degree. As shown in Table 1 and 2, the specific heat capacity increases with temperature at lower temperature ranges, but it tends to stabilize at higher temperatures. For CuF, Cp rises from 30.22 J/mole/K at 100 K to 38.28 J/mole/K at 2500 K. A similar trend is observed for CuCl, where Cp increases from 31.57 J/mole/K at 100 K to 38.30 J/mole/K at 2500 K. CuBr and CuI also show comparable trends, with the specific heat capacity increasing initially and then leveling off as temperature rises.

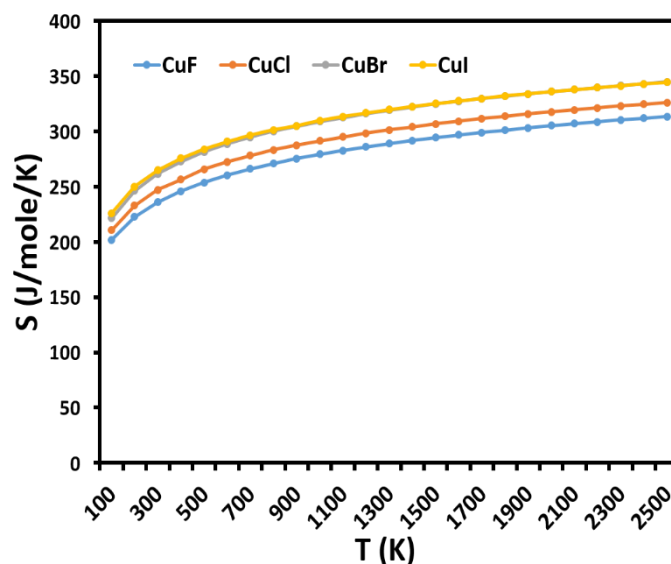


Fig. 3. Variation of Entropy (S) with temperature (T).

The increase in Cp at lower temperatures can be attributed to the gradual excitation of rotational and vibrational motions in the molecules. At lower temperatures, the heat capacity is dominated by translational motion, but as the temperature rises, the rotational and vibrational motions become more significant, leading to an increase in Cp. However, at higher temperatures, once most of the molecular motions have been excited, the specific heat capacity reaches a plateau and becomes nearly constant. This behavior is consistent with the Dulong-Petit law, which states that the heat capacity of solids tends to a constant value at high temperatures.

3.5. Spectroscopic Constants and Comparison with Observed Values

The spectroscopic constants, including the vibrational frequency (ω_e), anharmonicity constant ($\omega_e x_e$), and rotational constants (B_e and α_e), are presented in Table 3. These constants are essential for calculating the thermodynamic quantities, as they determine the energy levels of the molecules. The vibrational frequencies decrease as the size of the halogen atom increases, with CuF having the highest frequency (622.7 cm^{-1}) and CuI the lowest (264.5

cm^{-1}). This trend is expected, as larger atoms lead to lower vibrational frequencies due to their greater mass.

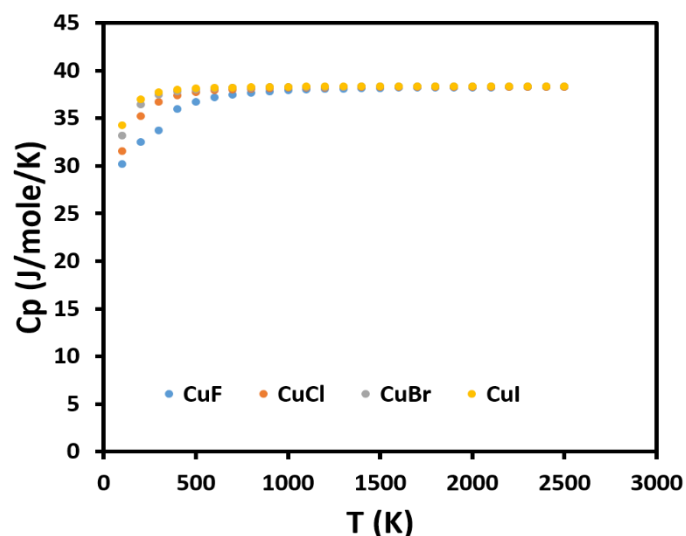


Fig. 4. Variation of Specific heat (C_p) with temperature (T).

The comparison between calculated and observed thermodynamic quantities at 300 K, as shown in Table 4, demonstrates excellent agreement for CuF, CuCl, and CuBr. The calculated entropy (S_{cal}) and specific heat capacity ($C_{p,\text{cal}}$) values are very close to the observed values (S_{obs} and $C_{p,\text{obs}}$), with deviations of less than 1%. This high level of agreement validates the accuracy of the computational methods used in this study.

The thermodynamic behavior of copper monohalides shows consistent trends across the different compounds. Free energy, enthalpy, and entropy all increase with temperature, reflecting the growing disorder and energy content within the system. Specific heat capacity increases at lower temperatures but stabilizes at higher temperatures, consistent with the excitation of molecular motions. The results demonstrate that while the halogen component influences the molecular weight and vibrational frequencies, it has a relatively minor impact on the overall thermodynamic properties of the copper monohalides.

This study provides a comprehensive understanding of the temperature-dependent thermodynamic behavior of copper monohalides, which is essential for their potential applications in materials science and nanotechnology. The results offer insights into the stability and energy dynamics of these molecules, laying the groundwork for further exploration of their use in high-temperature environments and advanced technologies.

4. CONCLUSION

The thermodynamic properties of copper monohalides—CuF, CuCl, CuBr, and CuI—have been effectively determined

using spectroscopic data and the partition function method, accounting for anharmonicity and nonrigidity effects. Our findings show a consistent variation of thermodynamic properties such as Gibbs free energy, enthalpy, entropy, and specific heat capacity over a temperature range of 100 K to 3000 K. These variations align with the rotational, vibrational, and translational motions of the molecules, offering a deeper understanding of the molecular dynamics of these compounds. This study not only provides essential data for theoretical models but also lays the groundwork for practical applications in advanced materials, nanotechnology, and smart material design. Future research can expand on these findings by incorporating additional spectroscopic data and exploring the influence of external factors such as pressure and magnetic fields on these thermodynamic properties.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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