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Thermodynamics Calculations of Diatomic Molecules Based on Morse Potential

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Abstract: The thermodynamic properties for some metal-containing (Cu, Fe, Pb, Cr, Sn, Ge) diatomic molecules were studied by density functional theory (DFT) method at B3LYP/6-311G(d,p) and B3LYP/SDD levels and statistical mechanical method based on Morse potential in 300K-5000K. Results show that the heat capacity and entropy obtained CuO, CuCl, FeO and CrO diatomic molecules are in a good agreement with reference data with the deviation of no more than $0.7(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$, and the entropy variations for GeX, SnX and PbX ($X = \text{S}, \text{Se}, \text{Te}$) are less than 0.75% in comparison with the reference data.

Key words: physical chemistry; diatomic molecule; Morse potential; density functional theory (DFT); thermodynamics property

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1 Introduction

The thermodynamic properties, such as the entropy and heat capacity, are the essential properties of compound. They are useful to describe processes that involve changes in temperature and transformation of energy and they are also important in aeronautics and space, astrophysical work, metallurgy, chemical engineering and ceramic industry^[1].

The thermodynamic properties of compound have been studied for many years^[2-4], however many experiments only reported about the nonmetallic compounds at solid state^[5-6] or in solution^[7] at low temperature. Recently many researchers have investigated the metallic molecules^[8-12]. But some of those results just provide the theoretical molecules spectroscopic information^[13]. Moreover, the Hartree-Fock self-consistent theory, semiempirical molecular orbital technique^[14] and the DFT treat the molecules approximately and there is an error of thermodynamic properties to the realistic state of the molecules although they may yield good experimental correlations for equilibrium bond lengths, frequencies and

optimized structure. However, it is difficult to calculate the thermodynamic properties of the metal-containing molecules accurately for high nuclear mass and the complex electronic structure of the metal atomic. This paper calculated the thermodynamic properties for some metal-containing diatomic molecules (some of them are the catalyst in solid rocket propellants) by using more realistic Morse potential approach in temperature range of 300 K to 5000 K.

2 Methodology and computational details

All calculations were performed with the Gaussian 03 software package^[15]. All optimizations, frequency calculations, and potential were performed using DFT, with Becke's three-parameter B3LYP functional. The molecular orbitals were expanded in a triple- ζ 6-311G basis augmented with single first d and p polarization functions for nonmetal atoms and lanl2dz basis set for metal atoms combined with relativ effective core potential (ECP).

Diatomic molecules are treated as the harmonic model in Gaussian 03 approach, and it can not represent the real state of the molecules in high temperature. Meanwhile it is time consuming to calculate the thermodynamic properties for the metal-containing molecules. Therefore, we treated the diatomic molecules as the anharmonic model by using Morse potential approximation, and calculated

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the thermodynamic properties of diatomic molecules based on Morse potential.

Generally, the feature of the ground state of all systems looks like an anharmonic model, thus the potential energy curves of diatoms molecules can be approached by Morse function^[16], such as

$$V(R) = D_e [1 - e^{-a(R-R_e)}]^2 + V_0, \quad a = \sqrt{\frac{k}{2D_e}} \quad (1)$$

Where D_e is the depth of the potential, k is the bond force constant, R is the distance between the nuclei of bonded atoms, R_e is the equilibrium internuclear distance. V_0 is the shift potential constant and is often chosen to be null.

The eigenvalues of Morse potential is :

$$E(n) = (n + 0.5)\omega_e - (n + 0.5)^2\chi_e\omega_e \quad (2)$$

Where ω_e is the harmonic vibrational frequency and $\chi_e\omega_e$ is the anharmonic constant, and

$$\chi_e = \frac{a^2 h}{2\mu\omega_e} = \frac{h\omega_e}{4D_e} \quad (3)$$

In addition, the atoms of rotating molecules are subject to centrifugal forces that tend to distort the molecular geometry and change the moments of inertia. For a diatomic molecule, the centrifugal distortion stretches the bond, and therefore increases the moment of inertia, the energy levels are less far apart than the rigid-rotor. So the rotational energy^[16] is expressed as (4) :

$$E(J) = BJ(J + 1) - 4B^3J^2(J + 1)^2/\omega_e^2 \quad (4)$$

Where J is the rotational quantum number, B is the rotational constant.

Ignoring the contribution from the electronic excitation energy to the thermodynamic properties while they are in ground state, the entropy and heat capacity from vibrational, rotational and translational motion were calculated. Here the statistical mechanical methods with partition functions((5)~(7)) was used to calculate the thermodynamic properties of the molecules^[17],

$$q_v = \sum_{i=0}^n e^{-E(i)/(kT)} \quad (5)$$

$$q_t = \frac{2\pi m k_B T}{h^2} \left(\frac{k_B T}{p} \right)^{3/2} \quad (6)$$

$$q_r = \sum_{i=0}^n g_i e^{-E(i)/(kT)}, \quad g = 2J + 1 \quad (7)$$

Where k_B is the Boltzmann constant and h is the Plank

constant. p is the standard pressure; g is the degenera- tion of the rotation; q_v, q_t , and q_r are the partition func- tion of vibrational, translational and rotational, respective- ly; E_{tot} is the total energy; $E(i)$ is the Morse potential energy or rotational energy :

$$E = \frac{1}{q} \sum_{i=1}^n E(i) e^{-E(i)/(kT)} \quad (8)$$

The heat capacity was calculated as :

$$C_{\text{tot}} = \frac{\partial E}{\partial T} = C_t + C_v + C_r = \frac{\partial E_t}{\partial T} + \frac{\partial E_v}{\partial T} + \frac{\partial E_r}{\partial T} \quad (9)$$

and the entropy was evaluated as follows :

$$S_{\text{tot}} = S_t + S_v + S_r + S_e = R(\ln q_t + \frac{5}{2}) + R(\ln q_v + T(\frac{\partial \ln q_v}{\partial T})) + R(\ln q_r + 1) + R \ln q_e \quad (10)$$

These equations was easily implemented into a simple Fortran routine to calculate the thermodynamic properties of the molecules.

3 Results and discussion

The ground electronic state of the CuO, CuCl, FeO and CrO diatomic systems was calculated with DFT method at B3LYP/6-311G(d,p) level to get the spectroscopic constants and the thermodynamic properties. The thermodynamic properties for the GeX, SnX and PbX (X = S, Se, Te) with the experimental spectroscopic constants was also calculated.

Figure 1 presents the heat capacity of CrO diatomic molecules calculated by Morse potential approach, B3LYP/6-311G(d,p) model and ECP method. The results from Morse potential are in a good agreement with the results from Reference [1], and results between Morse potential approach and B3LYP/6-311G(d,p) model is in good consistent, and the variations are no more than $0.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of CuCl at 2000 K and $0.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of CrO at 3000 K in comparison with reference data.

Table 1 - 2 list the heat capacity and entropy of GeO, SnO, PbO and CuO. Obviously, almost all the deviations of heat capacity obtained from Morse potential approach, harmonic oscillator model and DFT model are less 1% in comparison with the results of Reference [1], and the deviations of entropy are no more than 0.6%.

From results of the heat capacity and entropy for GeX, SnX and PbX (X = S, Se, Te), it is found that the deviations of entropy are less than 0.75%.

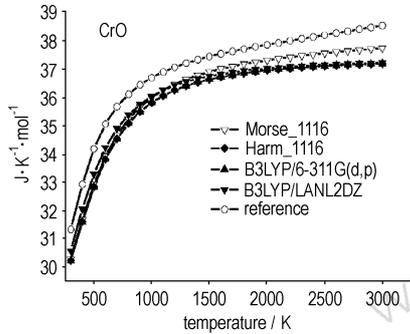


Fig. 1 Comparison of heat capacity of CrO calculated by different methods, the number 1116 are the frequencies calculated by DFT at B3LYP/6-311G(d,p) level

4 Conclusions

In this paper, Morse potential approach was presented

to treat the diatomic molecules as the anharmonic oscillator to evaluate the heat capacity and entropy of CuO, CuCl, FeO, CrO, as well as GeX, SnX and PbX (X = O, S, Se, Te) molecules. The results show that the Morse potential approach can be used to predict the thermodynamic properties for diatomic molecules in 300 – 2000 K (even at 5000 K). The results obtained from the Morse potential approach are in a good agreement with references for CuO, CuCl, FeO and CrO diatomic molecules with the deviation no more than $0.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and for the entropy of GeO, SnO, CuO and PbO, the deviation is less than 0.6%. In addition, the deviations of heat capacity and entropy of GeX, SnX and PbX (X = S, Se, Te) are within 0.75%. It is shown that the presented Morse potential approach is an efficient and accurate approach to calculate the heat capacity and entropy of the diatomic molecules in a large temperature range using the parameters of ω_e , $\chi_e \omega_e$, or D_e , B_e of the diatomic molecules.

Table 1 The heat capacity of the Cu, Sn and Pb oxides¹⁾

T/K	CuO				SnO				PbO			
	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]
300	30.85	30.78	30.76	31.00	31.85	31.76	32.10	31.60	32.54	32.44	32.51	32.5
400	32.4	32.30	32.28	33.74	33.47	33.36	33.67	33.45	34.11	33.99	34.05	34.12
500	33.64	33.53	33.51	35.01	34.59	34.46	34.73	34.37	35.13	34.98	35.02	35.15
600	34.56	34.43	34.41	35.71	35.36	35.21	35.42	34.90	35.80	35.62	35.67	35.82
700	35.22	35.07	35.06	36.12	35.89	35.72	35.89	35.27	36.25	36.05	36.08	36.28
800	35.71	35.54	35.53	36.39	36.27	36.07	36.21	35.55	36.57	36.34	36.37	35.61
900	36.08	35.89	35.88	36.58	36.56	36.33	36.45	35.77	36.81	36.55	36.57	36.85
1000	36.36	36.15	36.14	36.71	36.78	36.53	36.62	35.96	36.99	36.71	36.73	37.04
1100	36.58	36.35	36.35	36.81	36.94	36.67	36.75	36.12	37.14	36.82	36.84	37.19
1200	36.76	36.51	36.51	36.88	37.08	36.78	36.85	36.27	37.26	36.92	36.93	37.32
1300	36.91	36.64	36.63	36.94	37.19	36.87	36.93	36.42	37.36	36.99	37.00	37.42
1400	37.03	36.74	36.74	36.99	37.29	36.95	37.00	36.55	37.45	37.04	37.05	37.51
1500	37.13	36.82	36.82	37.02	37.38	37.00	37.05	36.68	37.53	37.09	37.10	37.59
1600	37.22	36.89	36.89	37.05	37.45	37.05	37.09	36.80	37.6	37.13	37.14	37.66
1700	37.30	36.95	36.94	37.08	37.52	37.09	37.13	36.92	37.66	37.16	37.17	37.7
1800	37.37	37.00	37.00	37.10	37.58	37.13	37.16	37.04	37.72	37.19	37.20	37.79
1900	37.44	37.04	37.04	37.12	37.63	37.16	37.18	37.16	37.78	37.21	37.22	37.84
2000	37.50	37.05	37.01	37.13	37.69	37.18	37.21	37.27	37.83	37.23	37.23	37.90
3000	38.04	37.35	37.34	-	37.68	37.32	37.32	-	37.71	37.33	37.33	-
4000	38.35	37.38	37.38	-	37.86	37.36	37.36	-	37.89	37.37	37.37	-
5000	38.68	37.39	37.39	-	38.02	37.38	37.38	-	38.05	37.39	37.38	-

Note: 1) Heat capacity in units of ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). 2) The Morse model in Fortran routine. 3) The harmonic oscillator model in Fortran routine. 4) At the B3LYP/6-311G(d,p) level for CuO and B3LYP/SDD for SnO and PbO. The experimental parameters (such as $\omega_e, \chi_e \omega_e, B_e$) obtained from reference [12] while calculating in Fortran routine.

Table 2 The entropy of the Cu, Ge and Pb oxides¹⁾

T/K	CuO				GeO				PbO			
	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]	Mor. ²⁾	Harm. ³⁾	DFT ⁴⁾	Ref. [1]
300	230.3	230.2	230.1	234.8	224.2	224.2	224.2	224.5	240.2	240.2	240.1	240.2
400	240.0	239.9	239.8	245.2	233.3	233.3	233.3	233.8	249.8	249.8	249.7	249.8
500	247.8	247.7	247.5	253.4	240.7	240.6	240.6	241.5	257.5	257.5	257.4	257.8
600	254.3	254.2	254.0	260.1	246.9	246.9	246.8	248.0	264.0	263.9	263.9	264.0
700	259.9	259.8	259.6	265.9	252.3	252.2	252.2	253.5	269.5	269.5	269.4	269.6
800	264.7	264.6	264.4	270.9	257.0	256.9	256.9	258.8	274.4	274.3	274.3	274.5
900	269.1	269.0	268.7	275.3	261.2	261.2	261.1	262.6	278.7	278.6	278.6	278.8
1000	273.0	272.8	272.6	279.3	265.0	265.0	264.9	266.5	282.6	282.5	282.4	282.7
1100	276.5	276.4	276.1	282.9	268.5	268.4	268.3	270.0	286.1	286.0	285.9	286.2
1200	279.8	279.6	279.3	286.2	271.7	271.6	271.5	273.2	289.3	289.2	289.1	289.5
1300	282.8	282.6	282.3	289.2	274.6	274.5	274.4	276.2	292.3	292.2	292.1	292.5
1400	285.5	285.3	285.0	292	277.3	277.3	277.2	278.9	295.0	294.9	294.8	295.2
1500	288.1	287.9	287.6	294.6	279.9	279.8	279.7	281.5	297.6	297.5	297.4	297.8
1600	290.6	290.3	290.0	297.1	282.3	282.2	282.1	283.9	300.0	299.9	299.8	300.3
1700	292.8	292.6	292.3	299.4	284.5	284.4	284.3	286.1	302.3	302.2	302.0	302.5
1800	295.0	294.8	294.4	301.6	286.6	286.5	286.4	288.2	304.4	304.3	304.2	304.6
1900	297.1	296.8	296.4	303.7	288.7	288.6	288.4	290.2	306.5	306.3	305.8	306.7
2000	299	298.7	298.3	305.6	290.6	290.5	290.3	292.1	308.4	308.2	308.1	308.7
3000	308.1	308.1	313.4	-	305.4	305.4	323.2	-	323.3	323.3	306.7	-
4000	318.9	318.9	324.2	-	316.2	316.2	333.9	-	334.1	334.1	317.4	-
5000	327.2	327.2	332.5	-	324.5	324.5	342.3	-	342.4	342.4	325.8	-

Note: 1) Entropy in units of ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). 2) The Morse model in Fortran routine. 3) The harmonic oscillator model in Fortran routine. 4) B3LYP/6-311G(d,p) level for CuO and B3LYP/SDD for GeO and PbO. The experimental parameters (such as $\omega_e, \chi_e, \omega_e, B_e$) obtained from reference [12] while calculating in Fortran routine.

References:

- [1] CHENG Nai-liang, NIU Si-tong, XU Gui-ying, et al. Barin. Thermodynamic data of pure substances[M]. Beijing: Science Press, 2003.
- [2] Boo W O, Stout J W. Heat capacity and entropy of CuF_2 and CrF_2 from 10 to 300 K, anomalies associated with magnetic ordering and evaluation of magnetic contributions to the heat capacity[J]. *J Chem Phys*, 1979, 71(1): 9–16.
- [3] Stølen S, Glockner R, Gronvold F, et al. Heat capacity and thermodynamic properties of nearly stoichiometric wustite from 13 to 450 K[J]. *American Mineralogist*, 1996, 81: 973–981.
- [4] Ben-Amotz D, Widom B. Generalized solvation heat capacities[J]. *J Phys Chem B*, 2006, 110: 19839–19849.
- [5] Dandekar D K, Tsou J J, Ho J C. Low-temperature heat capacities of orthorhombic and cubic PbF_2 [J]. *J Phys Rev B*, 1979, 20(8): 2523–2525.
- [6] Likhachev V N, Vinogradov G A. Anomalous heat capacity of nanoparticles[J]. *Phys Lett A*, 2006, 357: 236–239.
- [7] Safarov M M, Zaripova M A, Radzhabov F S. Thermal capacity of aqueous aeroxine solutions as a function of temperature and pressure [J]. *Measurement Techniques*, 1996, 39(5): 540–554.
- [8] Midda S, Bera N C, Bhattacharyya I, et al. Ab initio and density functional theory study of spectroscopic properties of CuO and CuS[J]. *J Mol Struct (theochem)*, 2006, 761: 17–20.
- [9] Jacobs M H, Hack K, Hallstedt B. Heat balances and heat capacity calculations[J]. *J Solid State Electrochem*, 2007, 11: 1399–1404.
- [10] Konings R J, Miltenburg J C, Genderen A C. Heat capacity and entropy of monoclinic Gd_2O_3 [J]. *J Chem Thermodynamics*, 2005, 37: 1219–1225.
- [11] Johari G P. Determining vibrational heat capacity and thermal expansivity and their change at glass-liquid transition[J]. *J Chem Phys*, 2007, 126: 114901–114904.
- [12] LI Quan, LU Hong, WANG Hong-yan, et al. The theoretical calculation of potential energy functions and thermodynamic functions for the ground state of PuN[J]. *Chinese Journal of Chemical Physics*, 2003, 16(2): 99–102.
- [13] Jalbout A F, Li X H. Analytical potential energy functions and theoretical spectroscopic constants for MX/MX_- ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$) and LuA ($\text{A} = \text{H}, \text{F}$) systems: density functional theory calculations[J]. *J Quantum Chem*, 2007, 107: 522–539.
- [14] Kayi H, Clark T. AM1* parameters for copper and zinc[J]. *J Mol Model*, 2007, 13: 965–979.
- [15] Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 03; Gaussian, Inc.: Pittsburgh, PA, 2003.
- [16] Atkins P W. Physical Chemistry[M]. Forth Edition. Oxford: Oxford University Press, 1990. Chapter 16.
- [17] www.gaussian.com/g_whitepap/thermo.htm[J/OL].

- of polymer-inorganic hybrid membranes [D]. Tianjing: Tianjing University, 2006.
- [14] 马秀芳. 高聚物粘结炸药结构与性能的计算模拟研究 [D]. 南京: 南京理工大学, 2006.
- MA Xiu-fang. Computational simulation study on structure and performance of polymer bonded explosives [D]. Nanjing: Nanjing University of Science & Technology, 2006
- [15] Allen M P, Tildesley D J. Computer Simulation of Liquids [M]. Oxford: Clarendon Press, 1987.
- [16] 于坤千, 李泽生, 李志儒, 等. 寡聚物在高分子母体中的扩散: 分子动力学模拟研究 [J]. 等学校化学学报, 2002, 23 (7): 1327 - 1330.
- YU Kun-Qian, LI Ze-Sheng, LI Zhi-Ru, et al. Diffusion of oligomeric penetrants in rubbery polymer matrixes: A study of simulation of molecular dynamics [J]. *Chemical Journal of Chinese Universities*, 2002, 23 (7): 1327 - 1330.

Molecular Dynamics Simulation of Plasticizer Diffusion

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Abstract: To overcome the disadvantage of experimental methods, plasticizer diffusion in the bond system of hydroxyl terminated polybutadiene (HTPB) propellant was simulated by the molecular dynamics (MD) method. The molecular models of plasticizer and the bond system were constructed in the software of Materials Studio 4.3. The mixture system performed geometry optimization was simulated under the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field. The mean square displaces of plasticizer in the bond system were obtained by statistical average. The plasticizer diffusion was obtained by Einstein equation. The diffusion coefficients ($10^{-4} \text{ cm}^2 \cdot \text{s}^{-1}$) of dioctyl sebacate (DOS) are respectively 0.0010, 0.0020, 0.0025, 0.0031, 0.0043 at the temperature of 273, 298, 310, 323, 348 K; and are respectively 0.0025, 0.0020, 0.0018, 0.0015 at the content of 23%, 37.5%, 47%, 60%. The results show that the diffusion coefficients gradually increase with increasing of environmental temperature and decrease a little with increasing of the DOS content.

Key words: physical chemistry; molecular dynamics simulation; plasticizer; bond system; diffusion

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基于 Morse 势函数的含金属双原子分子的热力学性能计算

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摘要: 采用密度泛函 B3LYP 方法在 6-311G(d,p)、LANL2DZ-6-311G(d,p) 和 SDD 水平上优化和计算了含金属 (Cu, Fe, Pb, Cr, Sn, Ge) 双原子分子的平衡几何结构、简谐振动频率和温度在 300 K 到 5000 K 时的热容和熵, 并采用自编的 Fortran 程序 (基于 Morse 势函数的方法), 计算了上述双原子分子的热容和熵。计算结果表明, 基于 Morse 势函数的方法得到的 CuO, CuCl, FeO 和 CrO 的热容和熵, 与文献中的结果一致, 其中最大偏差为 $0.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; 计算的 GeX, SnX 和 PbX (X = S, Se, Te) 的热容和熵与文献值的最大偏差为 0.75%。

关键词: 物理化学; 双原子分子; Morse 势; 密度泛函理论; 热容; 熵

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