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Molecular Dynamics Study on the Effect of Surface Adsorption on the Properties of JB-9014 Explosive

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Abstract

In order to explore the influence of gas adsorption on the performance of JB-9014 explosive, this paper simulated the gas adsorption on its (001), (010) and (100) three crystal surfaces, and calculated and analyzed by molecular dynamics method. The results showed that the adsorption stability of CO2, H2O and NH3 on the surface of explosive was stronger than that of N2 and CO. The cohesive energy density, van der Waals force and electrostatic force of the explosive decreased after gas adsorption, indicating that the sensitivity of the explosive increased after adsorption. Gas adsorption will make the explosive crystal isotropic, reduce the tensile modulus and shear modulus, and further reduce the fracture resistance and rigid strength of explosive materials.

Keywords

Physical chemistry; Surface adsorption; Molecular dynamics; Mechanical properties; Sensitivity.

1. Introduction

JB-9014 explosive is a polymer bonded explosive composed of TATB explosive and F_{2314} binder. JB-9014 explosive is currently widely used in strategic weapons. It is stored for a long time, and the explosive will undergo thermal decomposition in long-term storage. The released gas will be adsorbed on the surface of the explosive, which may affect the performance of the explosive. Therefore, it is of great theoretical significance and reference value to carry out the research on the influence of gas adsorption on the surface of JB-9014 explosive on its performance.

At present, Zhang Xiang et al [1] through the molecular dynamics simulation of multi-component gas adsorption on the surface of JOB-9003 explosive was carried out, the results show that the multi-component gas adsorbed on the surface of JOB-9003 explosive increases the impact sensitivity and thermal sensitivity of the explosive. Guo et al [2] studied the surface adsorption of JO-9159 explosive and found that the adsorption of gas on the surface of explosive would increase the sensitivity of explosive. Yu et al [3] used SPME (solid phase micro-extraction) technology to store JOB-9003 explosives and found that with the increase of temperature and storage time, the gas concentration of each component released by explosives showed an increasing trend. Bower J K et al [4] studied the effects of three polymers (Kel-F 800, phenoxy PKHJ and Kraton G 1650) on the properties of TATB explosives after adsorption, indicating that the three polymers changed the tensile and compressive properties of explosives to varying degrees.

In the study of JB-9014 explosives, Gao et al [5] studied the accelerated aging process of JB-9014 explosives through thermogravimetric analyzer and VLWR detonation program. Chi et al [6] studied the development of shock initiation pressure field of JB-9014 explosive at room temperature and low temperature by using manganese copper pressure gauge. Yu et al [7] used VISAR (dual-sensitivity laser interferometer) to measure the detonation performance of JB-9014 explosive in one-dimensional plane.

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Scholars at home and abroad have carried out some studies on JB-9014, but most of the studies are aimed at the detonation performance and mechanical properties under normal conditions, and there is a lack of research on the surface adsorption of JB-9014 explosives. Therefore, in this paper, for the surface adsorption of JB-9014 explosives, the surface adsorption model of JB-9014 explosives is established based on Langmuri adsorption model [8]. The surface adsorption mechanism of explosives is analyzed by radial distribution function (RDF) [9], and the sensitivity and mechanical properties are analyzed by MD method. The performance variation of JB-9014 explosive after surface adsorption was obtained.

2. Simulation Method of Surface Adsorption

2.1. Surface Adsorption model

The adsorption mathematical model used in this paper is Langmuri adsorption model, which has the following assumptions: 1 Each vacancy can only be adsorbed by one molecule; 2 All vacancy energies are equal; 3 The adsorption molecules on adjacent vacancies do not affect each other. The Langmuri adsorption expression under this adsorption model is as follows:

$$\theta_i = \frac{b_i p_i}{1 + b_i p_i} \tag{1}$$

$$b = \frac{1}{\sqrt{2\pi MKT}} \tag{2}$$

In the formulaθdenotes adsorption coverage; i Represents gas i; b is the Langmuri adsorption equilibrium constant; p is gas pressure, Pa; M is the amount of substance adsorbed by particles, mol; K is a Boltzmann constant; T is the temperature of adsorption system

2.2. Establishment of original model

JB-9014 explosive is composed of TATB and F_{2314} according to the mass percentage of 95:5[10]. F_{2314} (fluororubber) is composed of PVDF (polyvinylidene fluoride) and PCTFE (polyvinylidene fluoride) at a molar ratio of 1:4. Since JB-9014 belongs to mixed explosives, this paper uses the AC module in MS software to construct an amorphous model. According to the proportion of each component of explosives, 112 TATB molecules and 5 F_{2314} molecules are taken, and the density is set to 1.898 g/cm^3. Fig. 1 shows the component models and the JB-9014 explosive model.

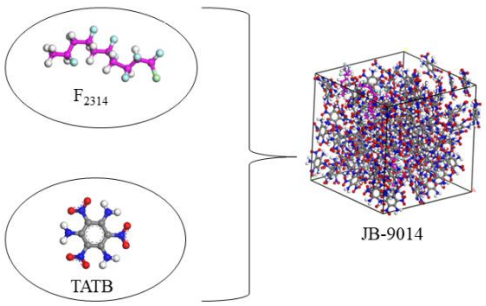

Fig. 1 Cell model of JB-9014

2.3. Model Verification

Tu et al [11] measured that the tensile modulus of JB-9014 was 5.86 GPa at 318 K. Therefore, eight amorphous models of JB-9014 were established in this paper. MD calculations were carried out at 318 K, and the tensile modulus obtained were 5.7963 GPa, 3.9871 GPa, 8.6889 GPa, 3.6089 GPa, 8.0545 GPa, 2.7014 GPa, 6.8525 GPa, 9.2638 GPa, respectively. The 5.7963 GPa model with the tensile modulus close to the literature value was selected as the original model.

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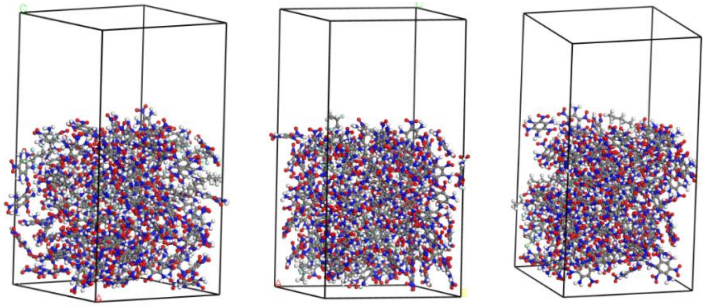
The verified crystal model was cut according to three planes (001), (010) and (100). After the cutting, a 2 nm vacuum layer was left in the Z-axis direction, as shown in Fig. 2.



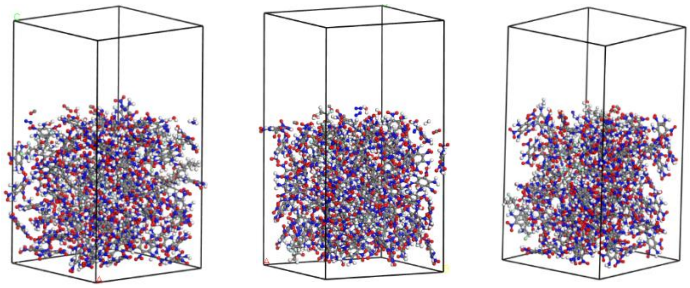
(a)(001) (b)(010) (c)(100)

Fig. 2 Cell model of different crystal planes

3. Mechanism of Gas Adsorption on JB-9014 Surface

3.1. Establishment of adsorption model

It can be seen from the literature [12] that under static conditions TATB thermally decomposed gas CO_2, N_2, CO, NH_3 and H_2O five gas molecules, so five thermally decomposed gas molecules were taken as adsorbates to adsorb on different crystal planes in this paper, as shown in Fig. 3.



(a)(001) (b)(010) (c)(100)

Fig. 3 Gas adsorption models of three crystal planes

In order to study the adsorption of gas molecules on the surface of JB-9014 explosive, by comparing the adsorption energy of different gas molecules on three crystal surfaces, the calculation formula of adsorption energy is:

$$\Delta E_{ad} = E_{total} - E_{JB\text{-}9014} - E_{gas} \quad (3)$$

In the formula ΔE_{ad} is the adsorption energy, the larger the absolute value, the more stable the structure formed, kJ; E_{total} is the total energy of the system, kJ; $E_{JB\text{-}9014}$ represents the total energy of explosives in the system, kJ ; E_{gas} represents the total energy of gas in the system, kJ.

Table 1 Adsorption energy of gas molecules on three crystal planes

JB-9014	(001)	(010)	(100)
ΔE_{ad} (kJ)	-635.031	-662.599	-672.114
E_{CO2} (kJ·mol^{-1})	-21.306	-21.285	-18.828
E_{N2} (kJ·mol^{-1})	-6.224	-13.152	-3.926
E_{CO} (kJ·mol^{-1})	-7.685	-8.778	-11.327
E_{NH3} (kJ·mol^{-1})	-26.459	-29.184	-29.690
E_{H2O} (kJ·mol^{-1})	-45.72	-40.172	-42.382

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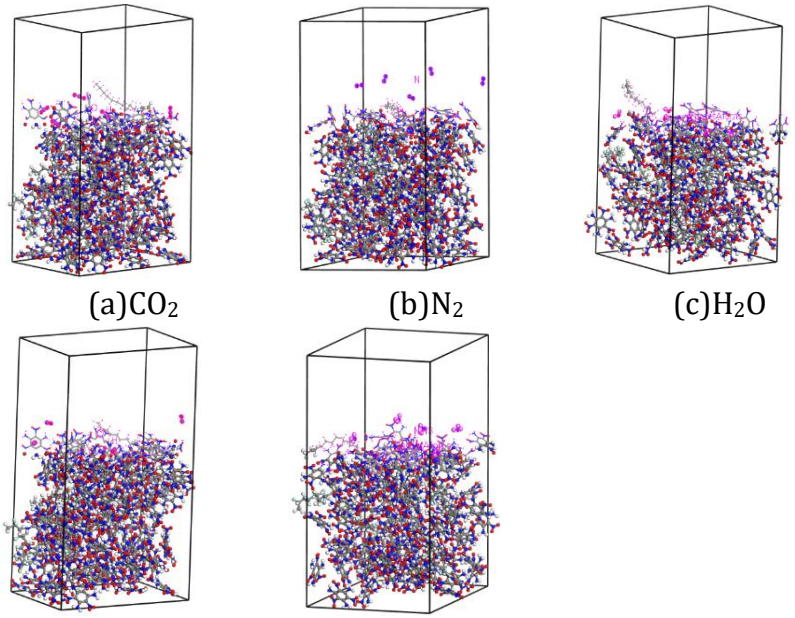
It can be seen from the Table 2 that the adsorption energy of gas on the three crystal planes of JB-9014 is negative, indicating that the adsorption process is exothermic and the adsorption is stable. The absolute value of adsorption energy on (100) plane is the largest, indicating that the structure formed after adsorption on (100) plane is the most stable. For the adsorption of different gas molecules on the same crystal surface, the adsorption energy on (001) surface is $E_{H2O} > E_{NH3} > E_{CO2} > E_{CO} > E_{N2}$. The adsorption energy on (010) surface is $E_{H2O} > E_{NH3} > E_{CO2} > E_{N2} > E_{CO}$; the adsorption energy on (100) surface is $E_{H2O} > E_{NH3} > E_{CO2} > E_{CO} > E_{N2}$. Therefore, the adsorption of CO_2, H_2O and NH_3 molecules on the surface of explosives is more stable than that of N_2 and CO molecules, which may be due to different adsorption mechanisms.

3.2. Molecular adsorption of single-component gas

In order to explore the reasons for the difference in the adsorption force of different gas molecules on the surface of JB-9014 explosive, five gas molecules were selected for adsorption on the surface respectively in this paper, and the reasons for the difference in the adsorption force were explained by studying the adsorption mechanism of gas molecules. The most stable (100) surface was selected as the adsorption object. The MD calculation of the adsorption model was carried out. The temperature was set to 295 K and the pressure was set to 0.0001 GPa. The calculation results are shown in Fig. 4.



(a)CO_2 (b)N_2 (c)H_2O

(d)CO (e)NH_3

Fig. 4 Model after MD calculation

The calculation results of molecular dynamics are analyzed by RDF, and the formula of radial distribution function $g(r)$ is:

$$g(r) = N_{ij} / \rho 4\pi r^2 \tag{4}$$

In the formula $g(r)$ is the measurement of the relative probability of finding j particle at the distance from the center particle r; N_{ij} is the number of particles j at the distance from r to $r + dr$ from the center particle i; ρ represents the average density of particle j.

At the microscopic scale, the interaction between particles is mainly van der Waals force and hydrogen bond. When the distance between the two particles is 0.26 ~ 0.31 nm, the hydrogen bond is hydrogen bond. r=0.31 – 0.50 nm is strong van der Waals force ; r > 0.50 nm is weak van der Waals force. Since the interaction force of hydrogen bonds is greater than van der Waals force, this paper mainly analyzes the C, O, N atoms with large electronegativity in the adsorbed gas and the H atoms on the surface of the explosive. As shown in Fig. 5 ~ 9, the radial distribution functions of the five adsorbed gases are shown.

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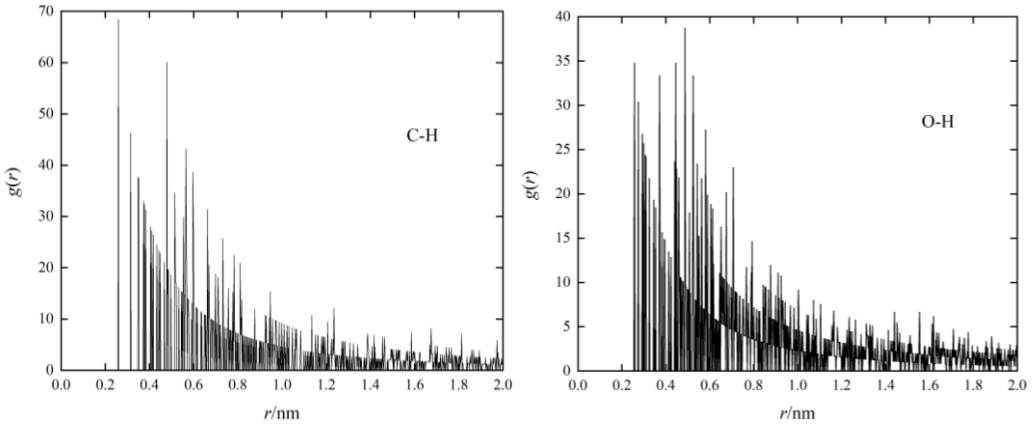

Fig. 5 RDF of C, O atoms in CO_2 and H atoms on explosive surface

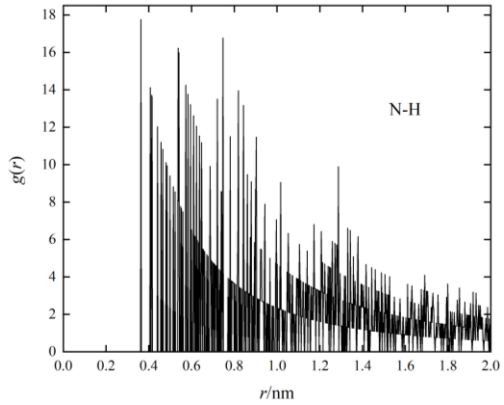

Fig. 6 RDF of N atoms in N_2 and H atoms on explosive surface

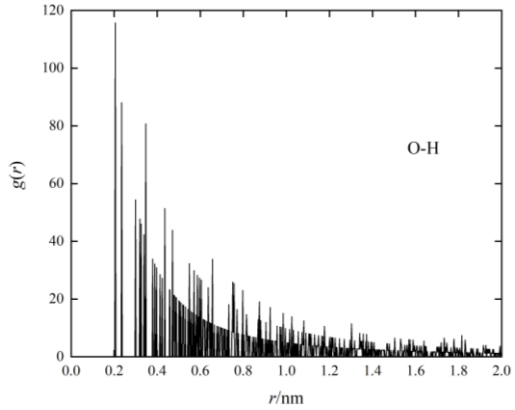

Fig. 7 RDF of O atoms in H_2O and H atoms on explosive surface

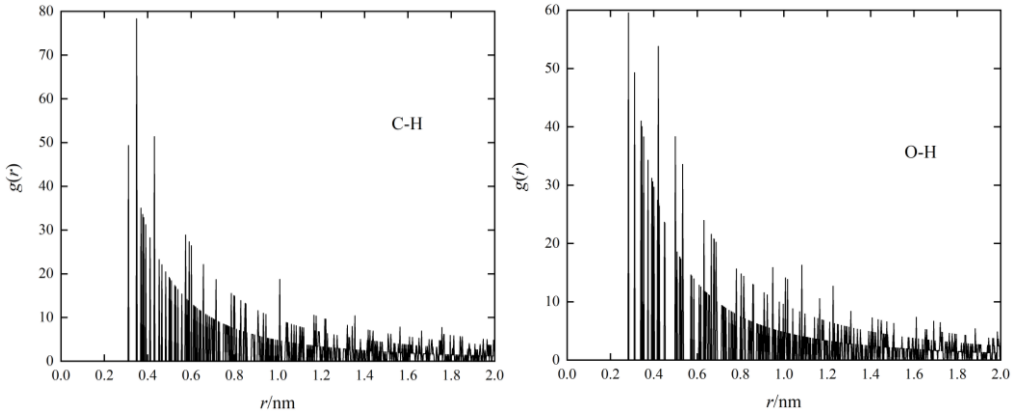

Fig. 8 RDF of C, O atoms in CO and H atoms on explosive surface

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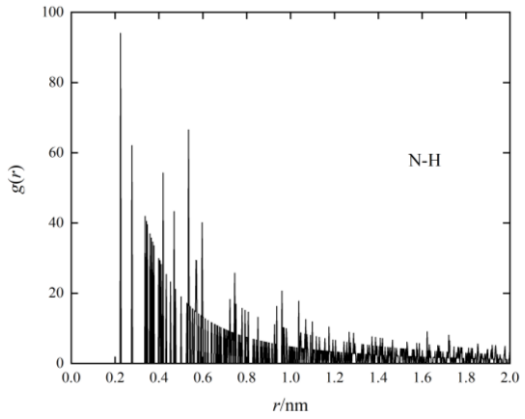

Fig. 9 RDF of N atoms in NH_3 and H atoms on explosive surface

From Fig. 5, it can be seen that the distance between C atoms in CO_2 and H atoms on the adsorption surface of JB-9014 explosive crystal is mainly distributed in the range of 0.26 ~ 0.81 nm, and their range of force includes hydrogen bond and van der Waals force ; the distance between O atoms and H atoms on the adsorption surface of explosive crystal in CO_2 is mainly distributed in the range of 0.26 ~ 0.67 nm, and their range of force includes hydrogen bond and van der Waals force. It can be seen from Fig. 6 that the distance between the N atoms in N_2 and the H atoms on the adsorption surface of the explosive crystal is mainly distributed between 0.36 nm and 0.86 nm, and the number of N atoms is less than that of other adsorbed gases. Their force range is only van der Waals force. From the Fig. 7, it can be seen that the distance between O atoms in H_2O and H atoms on the adsorption surface of explosive crystal is mainly distributed in the range of 0.21 ~ 0.78 nm, and their range of force includes hydrogen bond and van der Waals force. From the Fig. 8, it can be seen that the distance between C atoms in CO and H atoms on the adsorption surface of explosive crystal is mainly distributed in the range of 0.31 ~ 0.62 nm, and their force range is only van der Waals force ; the distance between O atoms in CO and H atoms on the adsorption surface of explosive crystal is mainly distributed in the range of 0.28 ~ 0.71 nm, and their force range includes hydrogen bond and van der Waals force. It can be seen from Fig. 9 that the distance between the N atoms in NH3 and the H atoms on the adsorption surface of the explosive crystal is mainly distributed between 0.22 nm and 0.97 nm, and their force ranges include hydrogen bonds and van der Waals forces.

From the above analysis, it can be seen that the reason for the small adsorption energy of N_2 and CO is that the N and C atoms in them have only van der Waals force in the range of H atoms on the adsorption surface of explosive crystal. The reason for the large adsorption energy of CO_2, H_2O and NH_3 is that the C, O and N atoms in them contain hydrogen bonds and van der Waals forces in the range of H atoms on the adsorption surface of explosive crystal, and the hydrogen bond force is stronger than van der Waals force.

4. Effect of surface adsorption on properties of JB-9014 explosive

MD calculations of three crystal adsorption models in Fig. 3 under normal environment were carried out. NPT ensemble and COMPASS force field were selected, the temperature was 295K, the pressure was 0.0001GPa, the time step was1fs, and the total step was 10000fs. Fig. 10 shows the temperature and energy balance trajectory of the (001) surface simulation process. It can be seen that after 4000 fs, temperature and energy gradually reach equilibrium, the equilibrium data as the basis for analysis.

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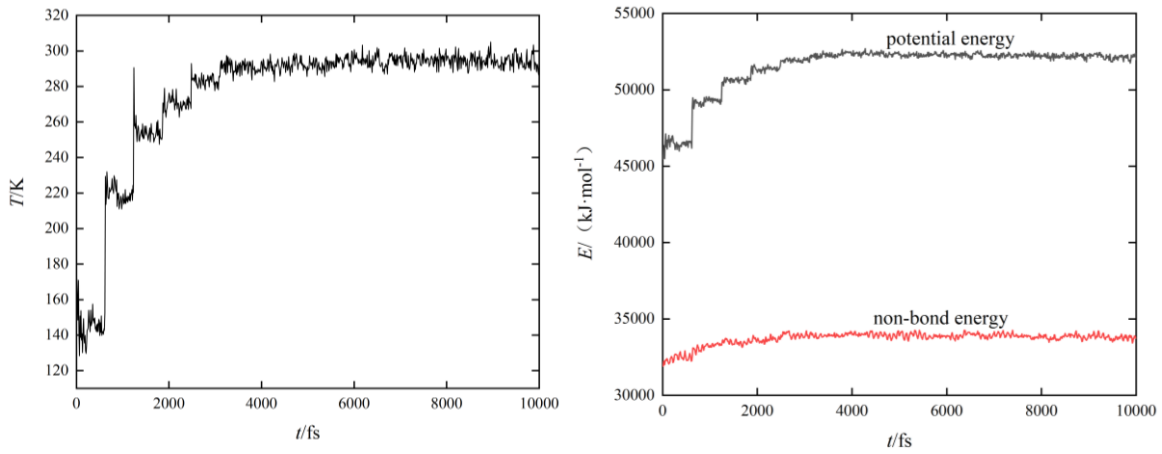

Fig. 10 Temperature and energy balance trajectory

4.1. Influence on cohesive energy density

Cohesive energy density (CED) refers to the energy required by 1 mol aggregates in unit volume to overcome the gasification of intermolecular forces. The calculation formula is:

$$\mathrm{CED} = \frac{\mathrm{H_V} - RT}{V_\mathrm{m}} \tag{5}$$

CED is cohesive energy density, kJ·cm^{-3} ; $\mathrm{H_V}$ is molar evaporation heat, kJ·mol^{-1} ; RT is the expansion work of material gasification, kJ·mol^{-1} ; V_m is molar volume, cm^3·mol^{-1}.

The cohesive energy density is numerically equal to the sum of van der Waals force (vdW) and electrostatic force, and its essence is a non-bond, which can reflect the strength of intermolecular interaction in the mixed system. The cohesive energy density, van der Waals force and electrostatic force of the three crystal systems before and after adsorption are calculated as shown in table 2.

Table 2 CED of three crystal planes of JB-9014 explosive

JB-9014		CED (kJ·cm^{-3})	vdW (kJ·cm^{-3})	electrostatic (kJ·cm^{-3})
(001)	Before	0.4358	0.2311	0.2047
	After	0.4119	0.2197	0.1922
(010)	Before	0.4160	0.2192	0.1968
	After	0.3970	0.2130	0.1840
(100)	Before	0.4203	0.2308	0.1995
	After	0.4166	0.2216	0.1950

It can be seen from the Table 2 that the energy needed to overcome the intermolecular force gasification after adsorption is less than that before adsorption, the difficulty of explosive explosion is reduced, indicating that the sensitivity of explosive increases. Before adsorption, the CED of (001) surface was the largest, and the CED of (010) surface was the smallest, indicating that the sensitivity (010) > (100) > (001).

4.2. Effect on mechanical properties

Static mechanical analysis of three crystal planes before and after adsorption was carried out, and the following formulas were obtained according to Hooke ' s law[13]:

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$$E = \frac{9KG}{3K + G} \tag{6}$$

In the formula, K is the bulk modulus, indicating the hardness of the material, GPa ; G is the shear modulus, indicating the fracture resistance of the material, GPa ; E is tensile modulus, representing the rigidity of the material, GPa.

JB-9014	(001)		(010)		(100)	
	Before	After	Before	After	Before	After
C_{11}	4.9771	3.3843	3.2491	2.1627	-0.3287	-0.9014
C_{22}	3.5307	2.5778	-0.8100	-0.7703	4.1264	1.8664
C_{33}	-0.7869	-0.0426	2.0479	1.5295	3.3727	0.2059
C_{44}	1.6334	0.8163	0.6705	0.2917	0.8659	0.5323
C_{55}	-0.3561	0.2939	1.0579	0.6938	0.7232	0.0595
C_{66}	1.1790	0.2557	1.6517	0.0821	0.2575	0.7448
C_{12}	1.4025	0.7685	-0.2080	0.1462	0.3130	-0.4350
C_{13}	-0.7723	0.0891	-0.1277	0.8622	-0.0110	0.2421
C_{23}	-0.4176	-0.3503	-0.4970	-0.4450	1.9222	0.0681
C_{15}	-0.4576	0.4053	0.0319	-0.2558	-0.0555	-0.6761
C_{25}	-0.6639	0.1808	0.1293	0.0177	-0.0514	-0.6008
C_{35}	-0.3397	-0.0438	-0.1005	-0.1236	-0.1906	-0.8109
C_{46}	-0.0075	0.1880	0.0495	-0.0795	-0.1001	0.0762
E	1.3503	1.0897	0.6691	0.5281	1.8908	0.3947
K	0.3852	0.4526	0.0964	0.2853	0.6455	0.0512
G	0.7373	0.4959	0.9751	0.2216	0.9344	0.9173

It cn be seen from the above table that the values of C_{11}, C_{22}, C_{33} and C_{44}, C_{55}, C_{66} groups with different crystal planes are quite different, indicating that the explosive system is anisotropic. C_{15}, C_{25}, C_{35} and C_{46} are close to 0, indicating that the explosive system tends to orthogonal system. The values of C_{11}, C_{22}, C_{33} and C_{44}, C_{55} and C_{66} groups before and after the adsorption of the same crystal plane showed a decreasing trend as a whole, and the difference between the two groups after adsorption became smaller, indicating that the explosive system transformed to isotropic after adsorption. The tensile modulus and shear modulus of the explosives decreased after adsorption, indicating that the rigidity and fracture resistance of the explosives decreased after adsorption. After adsorption, the bulk modulus increases on both (001) and (010) surfaces, and decreases on (100) surface. However, it is observed that the compression coefficient (reciprocal of bulk modulus) of the explosive model is very large during the calculation process. Therefore, the change of bulk modulus is mainly caused by the vacuum volume set during modeling.

5. Conclusion

(1) The adsorption stability of CO_2, H_2O and NH_3 in the thermally decomposed gas of JB-9014 explosive on its surface is stronger than that of N_2 and CO. The main reason is that there are both hydrogen bonds and van der Waals forces in the interaction between C, O and N atoms in them and H atoms on the explosive surface.

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(2) The gas adsorption on the surface of the explosive will reduce the cohesive energy density, van der Waals force and electrostatic force of the explosive. The decrease in the cohesive energy density indicates that the energy required for the gasification of the explosive is smaller and the sensitivity is increased.

(3) The adsorption of gas on the surface of explosive will make the explosive crystal transform to isotropic, and reduce the tensile modulus and shear modulus, thereby reducing the fracture resistance and rigid strength of explosive materials.

In the long-term storage process of JB-9014 explosive, the factors affecting its surface adsorption are complex. At present, the adsorption of different crystal faces is studied under isothermal pressure conditions, and some meaningful conclusions are obtained. However, under different temperature and pressure conditions, it is bound to affect the surface adsorption process, which is the focus of the next research.

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