Vibrational properties of cagelike diamondoid nitrogen at high pressure

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Under high pressure, a cagelike diamondoid nitrogen structure was lately discovered by first-principles structure researches. This newly proposed structure is very unique and has not been observed in any other element. Using density-functional calculations, we study the pressure effect on its vibrational properties. The Born effective charges are calculated, and the resulting LO–TO splittings of certain infrared active modes are beyond 20 cm^{-1}. We depict the Γ-point vibrational modes and find the breathing mode, rotational mode, and shearing mode. Frequencies of all the optical modes increase with pressure increasing. Moreover, the relation between the breathing mode frequency and the nitrogen cage diameter is discussed in detail. Our calculation results give a deeper insight into the vibrational properties of the cagelike diamondoid nitrogen.

Keywords: first principle calculation, infrared and Raman spectra, nitrogen

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1. Introduction

Nitrogen molecule is usually considered to be inert at ambient condition due to the strong N≡N triple bond, which is much stronger than the N–N single bond. This indicates that the single-bonded nitrogen compound is a high-energy-density material.[1] This feature provokes a number of researches in searching for singly bonded polymeric nitrogen.[2–5] The breakthrough took place in the cubic gauche nitrogen, which was first predicted theoretically and then confirmed experimentally.[3,6,7] The crystal structure of cubic gauche nitrogen can be viewed as a distorted simple cubic structure, in which each nitrogen atom forms three N–N single bonds with its nearest neighbors. After continuous efforts, a number of diverse nitrogen solids are proposed theoretically, including black phosphorus structure,[3] C*mcm* chain,[8] zigzag chain,[9] layered boat,[10] etc.

Recently, the cagelike diamondoid nitrogen (cd-N) was proposed by first-principles calculations.[11] Among the known polymeric nitrogen structures, the cd-N structure is most stable above 263 GPa. In this study we extend our understanding of the vibrational properties of cd-N using density functional theory (DFT) calculations. The cd-N structure is fully optimized using the Quantum-ESPRESSO code.[12] The PBE functional[13] and the ultrasoft pseudopotential[14] are used in our calculations. The cutoff energy of plane wave is set to 60 Ry (1 Ry = 13.605 eV), which is sufficient to ensure the convergence. The $8\times8\times8$ k-mesh is used for integration over the first Brillouin zone. The density functional perturbation theory is used to calculate Born effective charge (BEC), dielectric constant, and phonon properties.[15,16]

2. Crystal structure and factor group analysis

The cd-N structure is very unique. As shown in Fig. 1(a), it has a body-centred cubic structure with a cage composed of 10 nitrogen atoms.[11] Therefore, the N10 cage can be taken as a building block of the cd-N structure. We give the central N10 cage in Fig. 1(b). The 10 nitrogen atoms can be obviously divided into two parts: six bridge N atoms and four cage N atoms. The former atoms construct an octahedron and connect neighboring N10 cages along x, y, and z directions. The latter atoms are located out of the octahedron. If we add nitrogen atoms to the eight vertexes of the cube in Fig. 1(b), we will obtain a cubic diamond structure.[17] Therefore, each bridge N atom is covalently bonded with its three neighbors (two cage N atoms in this cage and one bridge N atom in neighboring cage). Each cage N atom is equally covalently bonded with its nearest neighboring bridge N atoms and forms a pyramid.

As shown in Fig. 1, the bond angle θ_{cbc} (the subscript represents cage–bridge–cage) is smaller than 120°. The shortest bond length is the distance between two bridge N atoms (d_{bb}), which connect two neighboring N10 cages. The bond length between bridge N and cage N (d_{bc}) is larger than d_{bb}. Therefore, the bond between two bridge N atoms is stronger than that between cage N atom and bridge N atom. Actually, the bridge N atom is in sp^2 hybridization with its neighbors, while the cage N atom is in sp^3 hybridization.[11] As is well known, in carbon allotropes, the sp^2 hybridization (graphene) is stronger than the sp^3 hybridization (diamond).

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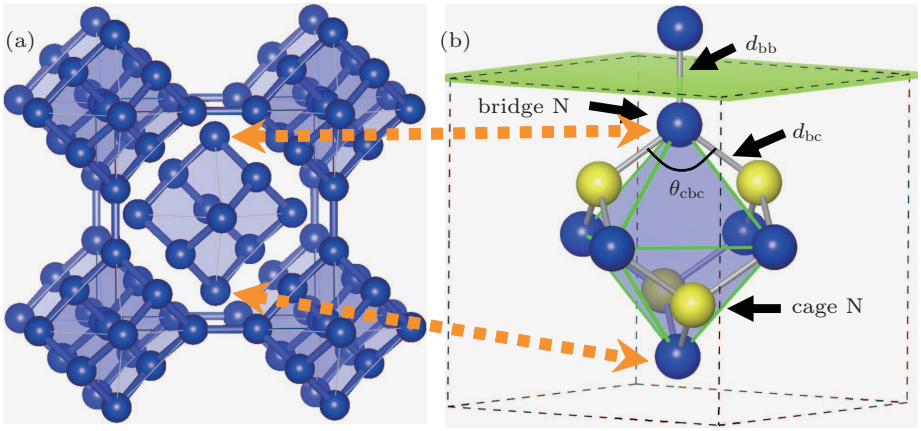


Fig. 1. (color online) Crystal structure of cagelike diamondoid nitrogen: (a) the conventional unit cell and (b) the N10 cage. There are six bridge N atoms and four cage N atoms in each N10 cage.

Because the cd-N structure is the most stable one in a pressure range from 263 GPa to 500 GPa,[11] we relax the structure in this pressure range. The lattice parameter under 300 GPa is 4.285 Å with nonequivalent nitrogen atoms sitting at (0.3532, 0, 0) and (0.6744, 0.6744, 0.6744), which accords well with the result in Ref. [11]. As shown in Fig. 2, the bond lengths of d_{bb} and d_{bc} decrease with the increase of isotropic pressure. However, the bond length difference (d_{bc}–d_{bb}) increases from 0.045 Å (240 GPa) to 0.052 Å (500 GPa). At the same time, the bond angle θ_{cbc} increases almost linearly with the increase of pressure. Therefore, isotropic pressure reduces the distance between nitrogen atoms, thereby making the cage N atoms close to the octahedral surfaces.

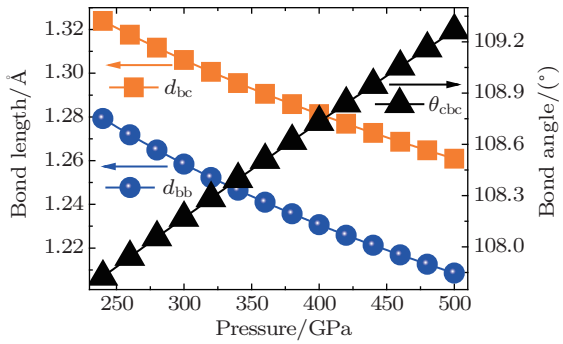


Fig. 2. (color online) Variations of bond lengths (d_{bb} and d_{bc}) and bond angle (θ_{cbc}) with isotropic pressure. The meanings of d_{bb}, d_{bc}, and θ_{cbc} refer to those in Fig. 1(b).

The factor group analysis is used to classify the vibrational modes of the cd-N structure at Γ point. Table 1 lists the representation operations and the number of atoms which remain invariant under symmetry operation. We find that there are two non-degenerate A_1 modes, two doubly degenerate E modes, three triply degenerate F_1 modes, and five triply degenerate F_2 modes at Γ point. Among them, one triply F_2 mode is acoustic mode and others are optical modes. The A_1 and E modes are Raman active and the F_2 modes are both Raman and infrared active.

Table 1. Characteristics of the irreducible representations of the T_d point group. $U(R, \tau_R)$ is the number of atoms which remain invariant under the operation (R, τ_R).

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Activity
A_1	1	1	1	1	1	Raman
A_2	1	1	1	–1	–1	none
E	2	–1	2	0	0	Raman
F_1	3	0	–1	1	–1	none
F_2	3	0	–1	–1	1	Raman & infrared
$U(R, \tau_R)$	10	1	2	0	4	
$\pm 1 + 2\cos\theta_R$	3	0	–1	–1	1	

3. Born effective charge of cd-N

Although cd-N structure is monatomic solid, the bridge N atom is different from the cage N atom. As a result, the Born effective charges (BECs) of nitrogen atoms are not zero. BECs and optical dielectric constant result into the LO–TO splitting of phonon.[18] The BEC is defined as the derivative of polarization with respect to the atomic displacement at zero macroscopic electric field.[19] Therefore, it is not a static but a dynamical quantity. It can also be understood as the ratio of the electric force acting on the ion to the electric field strength.[20]

The BECs of bridge N and cage N atoms are given in Fig. 3. The cage N atom has two independent components: Z^*_{c1} that is parallel to the three fold rotation axis and Z^*_{c2} that is perpendicular to this axis. Different from the cage N atom, the bridge N atom has three independent components. The first one (Z^*_{b3}) is parallel to the two fold rotation axes, the second one (Z^*_{b2}) lies in the plane composed of bridge N atom and two cage N atoms (cbc-plane), and the third one (Z^*_{b1}) is perpendicular to the cbc-plane. Pressure has little influence on the BECs and optical dielectric constant of cd-N structure. As seen from Fig. 3, Z^*_{c1} and Z^*_{b1} are negative and the others are all positive. As pointed in Ref. [11], the lone pair lob of

cage N points is opposite to the pyramid and that of bridge N is located at both sides of the cbc-plane. This means that all lone pair lobs avoid overlapping with their neighboring nitrogen atoms. When bridge N atom moves in the direction perpendicular to the cbc-plane, the lone pair lob moves in the same direction in order to reduce the overlap with neighboring atoms. However, when cage N atom moves in the cbc-plane, the lone pair lob moves in the direction opposite to it, thereby avoiding its overlapping with other atoms. It is the same for cage N atom. That is why Z^*_{c1} and Z^*_{b1} are negative and the other components are all positive.

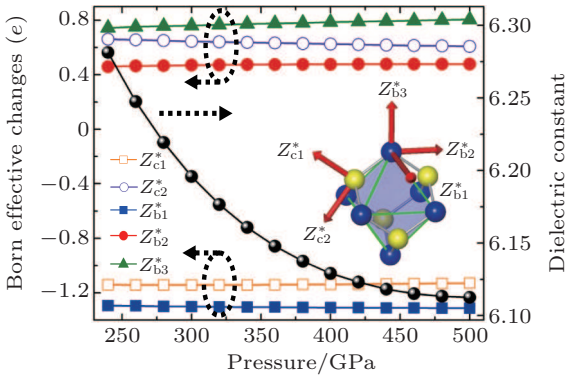


Fig. 3. (color online) Variations of optical dielectric constant and Born effective charges of bridge N (Z^*_b) and cage N (Z^*_c) with isotropic pressure. The right inset depicts the local rectangular coordinate systems used for bridge N and cage N atoms. Z^*_{b3} (Z^*_{c1}) is parallel to the two (three) fold rotation axes.

4. Vibrational properties of cd-N structure at Γ point

Raman and infrared spectra are widely used as a fast, cheap, and nondestructive method to investigate various kinds of materials.[21–25] The explaination of the experimental spectra relies on the calculation of phonon.[26–32] The factor group analysis shows that there are two A_1, two E, three F_1, and four F_2 optical modes at Γ point. However, this analysis does not take LO–TO splitting into account. As the BECs of cd-N are not negligible, each F_2 mode splits into one non-degenerate mode (LO mode) and one doubly degenerate mode (TO mode). The frequency of LO mode increases compared with that of TO mode.[18,19] Because the structure of cd-N is isotropic, there is no directional dispersion for the LO mode.

Using the BECs and optical dielectric constant given in Fig. 3, we take the LO–TO splitting into account and give the Γ-point phonon frequencies in Fig. 4. The highest frequency at 240 GPa is only 1612 cm^{-1}, which is much lower than the stretching mode frequency of N_2 molecule (2300 cm^{-1}–2500 cm^{-1}, depending on pressure).[4] There are four F_2 modes, which split into non-degenerate LO and doubly degenerate TO modes. For two F_2 modes around 900 cm^{-1} and 1100 cm^{-1}, the frequency differences between LO and TO modes are larger than 20 cm^{-1}. However, the LO–TO splitting has little effect on the other two F_2 modes, of which the LO–TO splittings are less than 4 cm^{-1}. Because the BECs and optical dielectric constant change slowly with pressure (referring to Fig. 3), pressure has little influence on the frequency difference between the LO and TO modes. It can be clearly seen from Fig. 4 that all the frequencies increase with pressure increasing. This is because the bond lengths of N–N decrease with the increase of pressure.

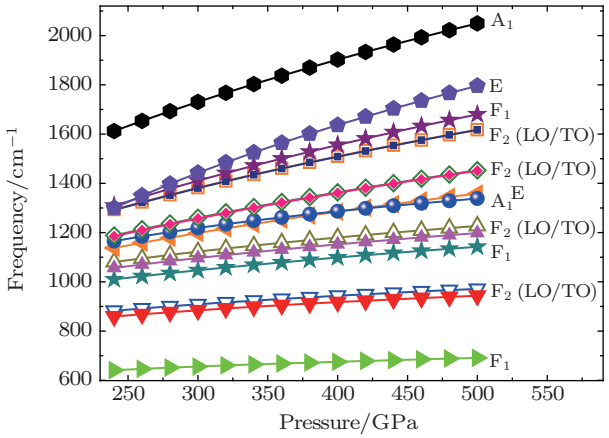


Fig. 4. (color online) Variations of Γ-point phonon frequencies with isotropic pressure. Open symbols (□, ◇, △, ▽) denote the LO modes and their corresponding solid symbols (■, ◆, ▲, ▼) represent the TO modes. The LO–TO splittings of two F_2 modes around 900 cm^{-1} and 1100 cm^{-1} are both larger than 20 cm^{-1} and those of other two F_2 modes are both very small.

In order to gain more insight into the phonon properties, we depict the optical vibrational modes of cd-N structure in Fig. 5. There is a rotational mode in Fig. 5(i), in which all nitrogen atoms rotate along the two fold rotation axes. It is neither Raman nor infrared active. In a molecule, frequency of a rotational mode is zero. But the N10 cage is not an isolated molecule. In the cd-N structure, two neighboring N10 cages are connected by two bridge nitrogen atoms. The N–N bond between bridge N atoms is strong. Therefore, the rotational mode of N10 cage can be viewed as a shearing vibration between nearest neighboring bridge N atoms. There is an F_2 mode in Fig. 5(j). It is obvious that the components of bridge N atom on the equatorial plane are very small. The other two bridge N atoms on the vertical apex move in the same direction. Therefore, this mode can be viewed as a shearing vibration of nonlinear three-atom molecule (one bridge N atom on the vertical apex and two cage N atoms).

The lowest frequency vibrational mode of Γ-point is depicted in Fig. 5(k). In this F_1 mode, four bridge N atoms move vertically and all cage N atoms move in the horizontal plane. It can be viewed as a combination of cage N atoms rotating

around the two fold rotation axes and bridge N atoms shearing in the direction parallel to the same axis. In this mode, two bridge N atoms on the opposite vertexes move in the same direction. This indicates that neighboring N10 cage has little influence on this mode. Therefore, it is a local vibrational mode of the N10 cage. That is why the frequency of this mode is slightly influenced by the pressure (referring to the bottom of Fig. 4).

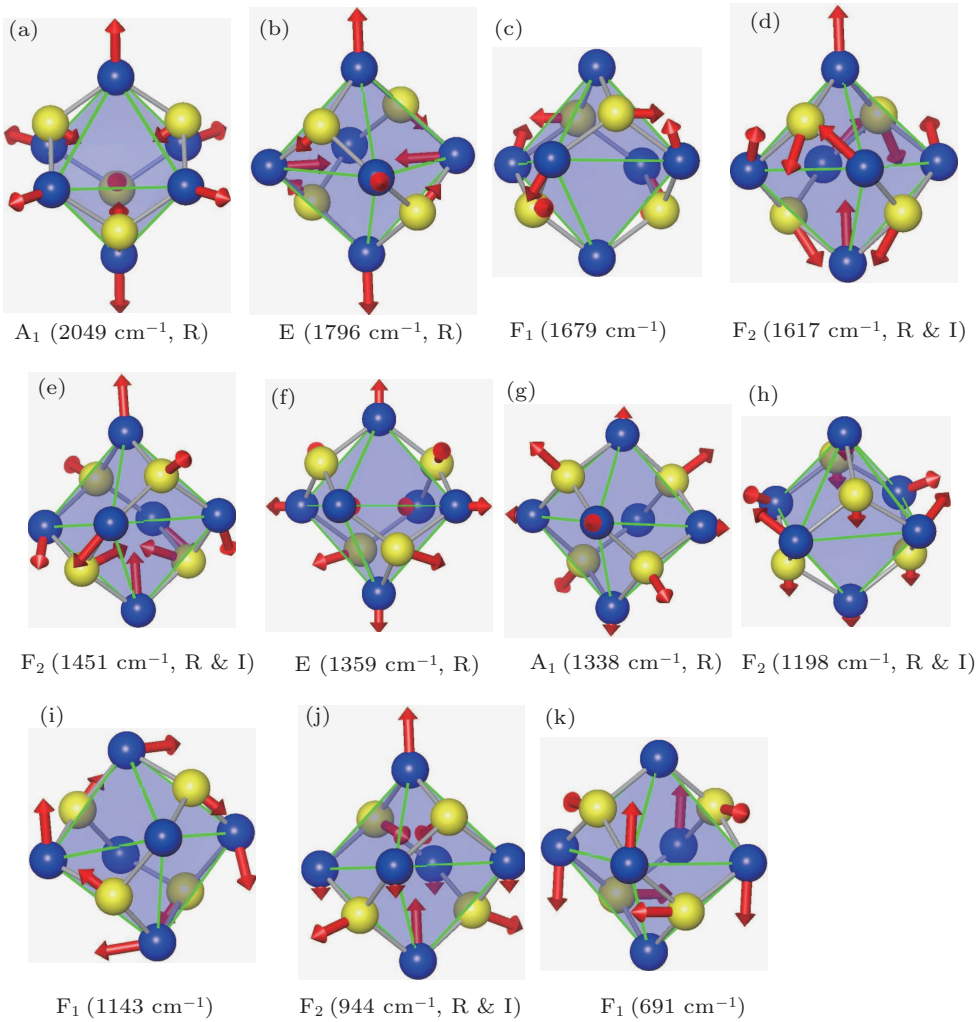


Fig. 5. (color online) Γ-point optical vibrational modes of cagelike diamondoid nitrogen. Arrows represent displacement directions. The frequencies in brackets are obtained under 500 GPa. The letters 'R' and 'I' represent 'Raman' and 'Infrared' activities, respectively.

There are two A_1 modes at Γ-point. One has the highest frequency (high-A_1 mode) and is shown in Fig. 5(a). In this mode, all cage nitrogen atoms move toward the center of octahedral, while all bridge nitrogen atoms move out of the center. The component of bridge N atom is bigger than that of cage N. The other A_1 mode is a breathing mode and depicted in Fig. 5(e). This A_1 mode is very interesting. The atomic displacement directions of the breathing mode are parallel with those of the high-A_1 mode. Different from the atoms in the high-A_1 mode, cage N and bridge N atoms in the breathing mode move in phase with each other and the component of bridge N atom is smaller than that of cage N atom. Therefore, the frequency of the breathing mode is smaller than that of the high-A_1 mode.

Breathing mode is usually the most important vibrational mode in Raman spectra. It exists in many materials, for example C_{60},[33] carbon nanotube,[27] BC_3 nanotube,[30] bct C4 structure,[17] etc. Similar to single-wall nanotubes, the cd-N structure[11] can be characterized using the breathing mode. We plot the variation of frequency of the breathing mode with N10 cage diameter in Fig. 6. With the increase of pressure, the size of the N10 cage decreases and the frequency of breathing mode decreases. The variation of N10 cage diameter totally originates from the change of N–N bond length. However, in carbon nanotubes, the increase of diameter results not from the change of bond length, but from the number of atoms in-

creasing. Therefore, the frequency–diameter relation for cd-N structure is different from that for single-wall nanotubes.[27,30]

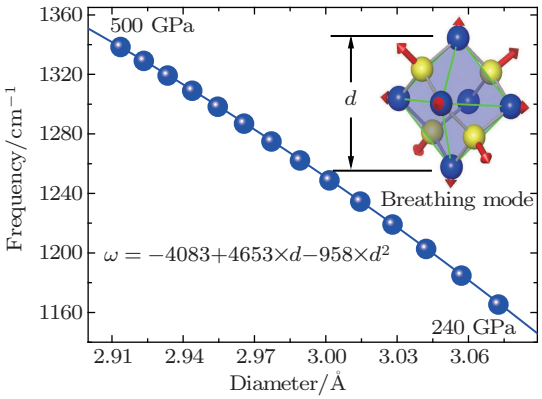


Fig. 6. (color online) Variation of breathing mode frequency with N10 cage diameter. The inset shows the vibrational mode, in which d represents the N10 cage diameter. The solid curve is the fitted relation between frequency (ω) and diameter (d).

5. Conclusions

In this paper, according to the density functional calculations, we give a detailed study of the structure, Born effective charges and vibrational properties of cagelike diamondoid nitrogen. Although the cagelike diamondoid nitrogen is monatomic solid, the Born effective charges are not negligible, owing to its special structure. We depict all the optical vibrational modes of Γ point and find breathing mode, rotational mode, and shearing mode. Based on the Born effective charges, the calculated LO–TO splittings of two F_2 modes are beyond 20 cm^{-1}. Furthermore, we demonstrate that all the frequencies increase with isotropic pressure increasing. As the breathing mode is very important in Raman spectrum, we discussed the variation of frequency of this mode with the diameter of N10 cage and gave a fitted relation. All these analyses are a step forward to further understanding the vibrational properties of the cagelike diamondoid nitrogen.

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