STUDY ON MECHANICAL AND THERMODYNAMIC PROPERTY OF MOLECULAR CRYOCRYSTALS CO_2 AND N_2O UNDER PRESSURE

NGUYEN QUANG HOC, HOANG VAN TICH

Hanoi National University of Education, Xuan Thuy, Cau Giay, Hanoi

NGUYEN DUC HIEN

Tay Nguyen University, 457 Le Duan, Buon Me Thuot City

Abstract. *The mechanical and thermodynamic properties (such as the nearest neighbor distance, the molar volume, the adiabatic and isothermal compressibilities, the thermal expansion coefficient, the specific heats at constant volume and at constant pressure) of some cryocrystals of many atoms with face-centered cubic structure such as $\alpha\text{-}CO_2$, $\alpha\text{-}N_2O$, at various temperatures and pressures up to 10 GPa are investigated by the statistical moment method (SMM) in statistical mechanics and compared with the experimental data.*

I. INTRODUCTION

Molecular crystals are characterized by strong intramolecular forces and much weaker intermolecular forces. Therefore, a molecule in the crystal retains its identity to a great extent Nevertheless, these solids represent the next progression in complexity from the monoatomic inert gas solids.

High-pressure spectroscopic studies provide useful data for refining the various model potentials which are used for prediction of the physical properties of such systems as well as for the formation of various crystalline phases [1]. These studies on molecular crystals also offer quite interesting aspects concerning the shape and nature of different types of forces. In high-pressure data provide a stringent test of various potentials which have been derived and tested mainly on the basis of temperature dependent properties of these solids at ambient pressure.

CO_2 is an important volatile component of the earth as well as other planets in the solar system. Its high-pressure behavior is therefore of fundamental importance in planetary science. On condensation into the solid state CO_2 forms a simple molecular crystal. The crystalline structure of such solids is mainly determined by weak intermolecular interactions, while the molecule itself is held together by strong intramolecular forces. From the fundamental point of view, CO_2 is one of the model systems involving the bonding and the hybridization properties of the carbon atom, which are strongly affected by the high pressure conditions [2].

The pressure-induced transitions from molecular to nonmolecular CO_2 crystals are systematically investigated by using first-principle lattice dynamics calculation. Geometrically, likely transition pathways are derived from the dynamical instability of the molecular crystals under high pressures [3]

According to [4, 14], the phase diagram of CO_2 composes 5 phases. CO_2-I (phase I or phase α known as dry ice) has the face-centered cubic $Pa3$ structure. CO_2-II has the $P42/mnm$ symmetry. CO_2-III has the orthorhombic $Cmca$ symmetry. CO_2-IV has $Pbcn$ symmetry. CO_2-V is the polymeric phase of tridymite-like structure. In [5], Bonev *et al.* performed a series of first principles calculations, including full structural optimizations, phonon spectra and free energies in order to study the stability and properties of the phases proposed experimentally up to 50 GPa and 1500 K. The DFT calculations were carried out within the Perdew-Burke-Ernzerhof [6] generalized gradient approximation (CGA) using the ABINIT code [7] which implements plane-wave basis sets[8]

. LeSar et al. presented an ab initio method, based on the modified Gordon-Kim (MGK) electron-gas model[9] that worked well in calculating the structure and properties of molecular crystals [10]

A combination of *ab initio* molecular dynamic simulations and fully relaxed total energy calculations is used to predict that molecular CO_2 should transform to nonmolecular carbonat phases based on CO_4 tetrahedra at pressures in the range of 35 to 60 GPa [11].

A constant pressure Monte Carlo formalism, lattice dynamics and classical perturbation theory are used to calculate the thermal expansion, pressure-volume relation at room temperature, the temperature dependence of zone center libron frequencies and the pressure dependence of the three vibron modes of vibration in solid CO_2 at pressures $0 \leq p \leq 16$ GPa and temperatures $0 \leq T \leq 300$ K[12]. Properties of solid N_2O at pressures 15 GPa and at and 300K have been calculated using energy optimization, Monte Carlo methods in an ensemble with periodic, deformable boundary conditions and lattice dynamics [13]. According to [15], α-N_2O is consistent with the known low-pressure low-temperature ordered cubic form, space group *Pa3*, up to 4.8 GPa where transition to a new solid occurs.

Cryocrystals N_2O and CO_2 are ideal systems on which to have a study of the influence of quantum effects on condensed matter. Up to now , there has been considerable interest in structural and thermodynamic properties of these crystals under temperature and pressure. In line with this general interest and encouraged by the essential success of our calculations, as applied to other substances [1], we tried to consider the mechanical and thermodynamic properties (such as the nearest neighbor distance, the molar volume , the adiabatic and isothermal compressibilities, the thermal expansion coefficient, the specific heats at constant volume and at constant pressure) of some cryocrystals of many atoms with face-centered cubic structure such as α-N_2O, α-CO_2 at various temperatures and pressures up to 10 GPa are investigated by the statistical moment method (SMM) in statistical mechanics and compared with the experimental data. Specifics heat at constant volume for these crystals are studied by combining the SMM and the self- consistent field method taking account of lattice vibrations and molecular rotational motion [16].

II. MECHANICAL AND THERMODYNAMIC PROPERTY FOR α-CO$_2$ AND α-N$_2$O CRYOCRYSTALS AT PRESSURE $p = 0$

It is known that the interaction potential between two atoms in α phase of molecular cryocrystals of N_2 type such as solids N_2, CO, CO_2 and N_2O is usually used in

the form of the Lennard-Jones pair potential

$$\phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{1}$$

where σ is the distance in which $\phi(r) = 0$ and ε is the depth of potential well. The values of the parameters ε, σ are determined from experiments. $\varepsilon/k_B = 218.82$K, $\sigma = 3.829.10^{-10}$ m for α-CO$_2$ and $\varepsilon/k_B = 235.48$K, $\sigma = 3.802.10^{-10}$ m for α-N$_2$O [20]. Therefore, using the coordinate sphere method and the results in [17], we obtain the values of parameters for α-CO$_2$ and α-N$_2$O as follows

$$k = \frac{4\varepsilon}{a^2} \left(\frac{\sigma}{a} \right)^6 \left[265.298 \left(\frac{\sigma}{a} \right)^6 - 64.01 \right],$$

$$\gamma = \frac{16\varepsilon}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[4410.797 \left(\frac{\sigma}{a} \right)^6 - 346.172 \right],$$

$$\gamma_1 = \frac{4\varepsilon}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[803.555 \left(\frac{\sigma}{a} \right)^6 - 40.547 \right], \tag{2}$$

$$\gamma_2 = \frac{4\varepsilon}{a^4} \left(\frac{\sigma}{a} \right)^6 \left[3607.242 \left(\frac{\sigma}{a} \right)^6 - 305.625 \right],$$

where a is the nearest neighbor distance at temperature T. At temperature 0K, the parameters of α-CO$_2$ and α-N$_2$O are summarized in Table 1. Our calculated results for the nearest neighbor distance a, the adiabatic and isothermal compressibilities χ_T, χ_S, the thermal expansion coefficient β and the specific heats at constant volume and constant pressure C_V, C_p of α-CO$_2$ and α-N$_2$O at different temperatures and pressure $p = 0$ are shown in [17]. In general, our calculations are in qualitative agreement with experiments.

III.   MECHANICAL AND THERMODYNAMIC PROPERTY FOR α-CO$_2$ AND α-N$_2$O CRYOCRYSTALS UNDER PRESSURE

In order to determine the thermodynamic quantities at various pressures, we must find the nearest neighbor distances. The equation for calculating the nearest neighbor distances at pressure P and at temperature T has the form [17]

$$y^2 = 1.1948 + \left[0.1717 + 0.0862 \frac{\theta}{\varepsilon} xcthx \right] y^4 - 0.0087 \frac{p\sigma^3}{\varepsilon} y^5 - 0,0019 \frac{\theta}{\varepsilon} xcthxy^6 + 0.0021 \frac{p\sigma^3}{\varepsilon} y^7, \tag{3}$$

where $y = \left(\frac{a}{\sigma} \right)^3, \theta = k_B T (k_B$ is the Boltzmann constant), $x = \frac{\hbar\omega}{2\theta}$ This is a nonlinear equation and therefore, it only has approximate solution. From that, the equation for calculating the nearest neighbor distances at pressure P and at temperature 0K has the form

$$y^2 = 1.1948 + 0.1717y^4 - 0..0087 \frac{p\sigma^3}{\varepsilon} y^5 + 0.0021 \frac{p\sigma^3}{\varepsilon} y^7. \tag{4}$$

After finding the solution $a(p,0K)$ from (4), we can calculate $a\ (p,T)$ and other thermodynamic quantities. This means is applied to crystal at low pressures. For crystal at high pressures, we must directly find the solution from (4).

For example in the case of α-CO_2 at $p = 0.5$ kbar, $T = 0K$, (4) becomes

$$y^2 = 1.1948 + 0.17y^4 - 0.00807y^5 + 0.082y^7. \tag{5}$$

The solution of this equation is $y = 1.281967$, i.e. the nearest neighbor distance under the condition $p = 0.5$ kbar, $T = 0K$ takes a value m. At temperature 0K and pressure p, the parameters of and α-N_2O are summarized in Table 2. Our calculated results for thermodynamic quantities of α-CO_2 and α-N_2O at different temperatures and pressures are shown in Figures 9 19. According to the experimental data, α-CO_2 exists in the pressure range of 0 to 12 GPa and in the temperature range of 0 to 120 K and α-N_2O exists in the pressure range of 0 to 4.8 GPa and in the temperature range of 0 to 130 K. Our numerical results are carried out in these ranges of temperature and pressure. We only have the experimental data for the phase diagram and the molar volume of α-CO_2 and α-N_2O under pressure. The dependence of thermodynamic quantities on temperature for α-CO_2 and α-N_2O crystals under pressure is in physical agreement with that at zero pressure. Our results will be more consistent with experiments by taking account of molecular rotation and intermolecular motion.

Table 2. Parameters of α-CO_2 and α-N_2O at $p = 0.5$ kbar, 1 kbar and $T = 0K$

Crystal	p	k	ω	γ	γ_1	γ_2	a_0
	kbar	J/m^2	$10^{13}s^{-1}$	$10^{21}J/m^2$	$10^{21}J/m^2$	$10^{21}J/m^2$	$10^{-10}m$
α-CO_2	0.5	4.1687	2.2869	2.3117	0.1108	0.4671	4.1578
	1	4.4444	3.3613	2.4559	0.1176	0.4964	4.1430
α-N_2O	0.5	4.5225	2.3649	2.5446	0.1220	0.5141	4.1299
	1	4.7967	2.4356	2.6900	0.1288	0.5437	4.1163

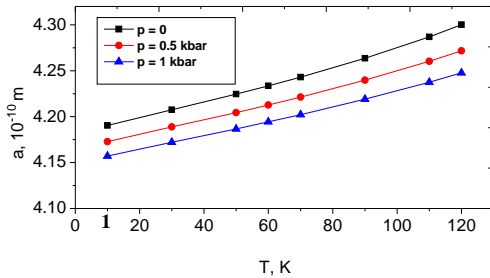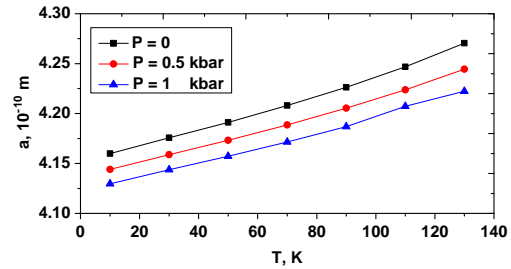Figure 1. Graphs for α-CO_2 at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar

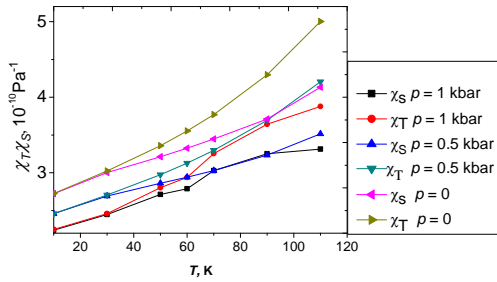Figure 2 . Graphs for α-N_2O at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar

Figure 3. Graphs χ_T (curves 1,3,5) and χ_S (curves 2,4,6) for α-CO_2 at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar
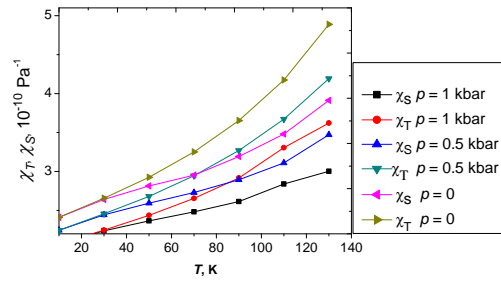
Figure 4. Graphs χ_T (curves 1,3,5) and χ_S (curves 2,4,6) for α-N_2O at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar
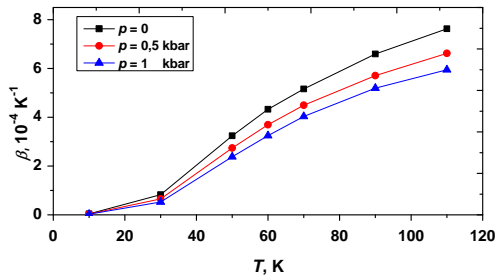
Figure 5. Graphs $\beta\omega T\omega$ for $-CO_2$ at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar
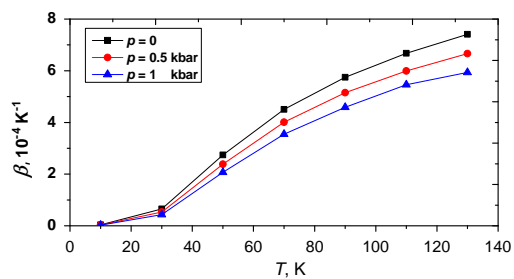
Figure 6. Graphs $\beta\omega T\omega$ for α-N_2O at $p = 0$, $p = 0.5$ kbar and $p = 1$ kbar
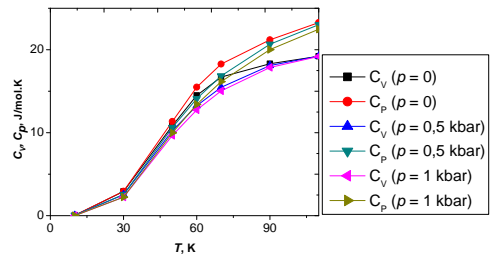
Figure 7. Graphs $C_V(T)$, $C_p(T)$ for α-CO_2 at p = 0, p = 0.5 kbar and p = 1 kbar
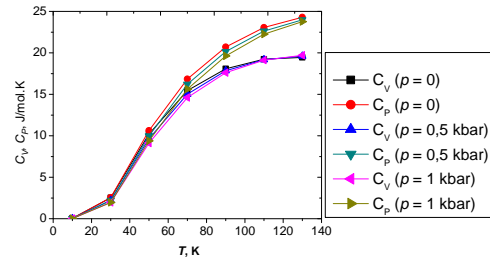
Figure 8. Graphs $C_V(T)$, $C_p(T)$ for α-N_2O at p = 0, p = 0.5 kbar and p = 1 kbar
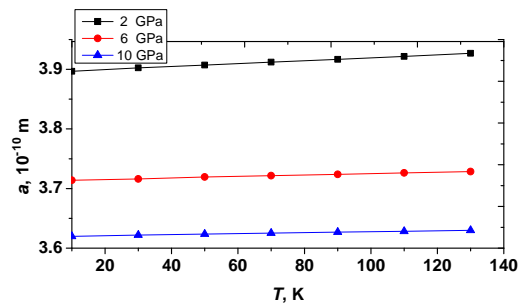
Figure 9. Graphs $a(T)$ for α-CO_2 at $p = 2$ GPa, $p = 6$ GPa and $p = 10$ GPa
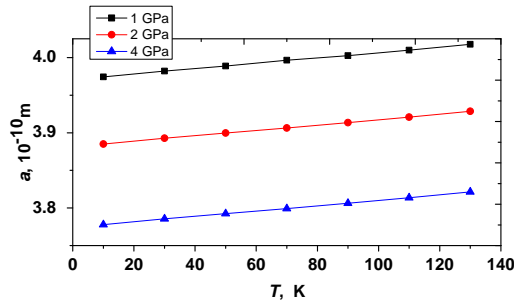

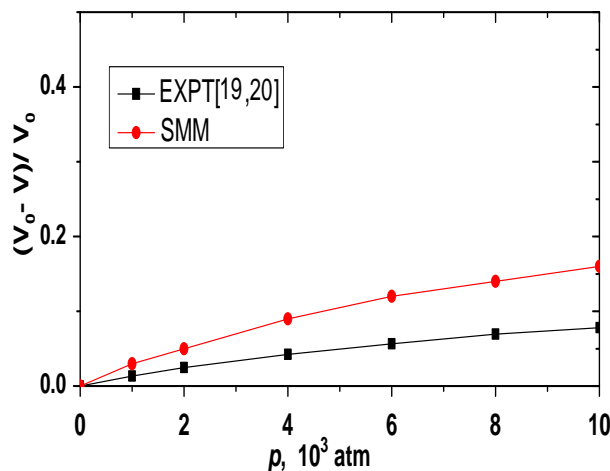Figure 10. Graphs $a(T)$ for α-N_2O at $p = 1$ GPa, $p = 2$ GPa and $p = 4$ GPa

Figure 11. Dependence of relative change of molar volume on pressure
at temperature 77 K for α-CO_2.

ACKNOWLEDGMENT

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