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Crystal structures of N₂O to 12 GPa by x-ray diffraction

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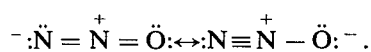
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The structures and phase transitions of N₂O were studied by powder x-ray diffraction in a tungsten-carbide anvil device from about 100 to 300 K and 2 to 12 GPa. Two solid phases, α -N₂O and β -N₂O, were observed. The α pattern is consistent with the known low-pressure low-temperature ordered cubic form, space group Pa3, up to 4.8 GPa where transition to a new β solid occurs. From refinements using photographic x-ray intensities, the β -N₂O structure was determined to be orthorhombic Cmca. There are four molecules in a unit cell with $a = 4.954$ Å, $b = 4.497$ Å, and $c = 6.201$ Å at 5.81 GPa and 298 K. The molecular axes lie parallel to the bc plane and are tipped at an angle of 37.2° to the b axis. Random head-to-tail orientation is probable in both solids. The phase diagram and values of the molar volume for N₂O are compared with published data for the isoelectronic molecule CO₂. Recent theoretical calculations correctly predict the β -N₂O structure.

INTRODUCTION

Nitrogen and carbon monoxide form an intriguing pair of diatomic molecules with almost identical charges and masses. Studies¹ of N₂ and CO under pressure have yielded information about the way subtle differences in intermolecular forces can affect physical and chemical behavior. The addition of one oxygen atom to N₂ and to CO produces another interesting pair of isoelectronic molecules, triatomic N₂O and CO₂. Whereas carbon dioxide has been studied extensively at high pressure, there is a paucity of complementary data on nitrous oxide.

Infrared absorption spectra² show that N₂O is linear, but unlike CO₂ the molecule is asymmetric with the two nitrogen atoms adjacent. Nitrous oxide represents a classic example of a molecule that resonates between two valence-bond structures with different bond distributions.³



Even though the resonance energy confers extra stability on the molecule, the oxygen atom is still so loosely bound that N₂O acts as a ready oxidizing agent, and supports combustion.

Resonance theory³ yields distances of 1.12 Å for N–N and 1.19 Å for N–O, the sum of which agrees exactly with the spectroscopic value⁴ 2.31 Å. The opposed electric dipole moments of the two resonating structures tend to cancel each other, leading to a total moment very near zero.⁵ Lacking a strong polarizing force, the molecules are randomly oriented end-for-end when they solidify in a cubic form^{6–11} at low pressure, and this randomness remains largely frozen in down to zero Kelvin where the entropy¹² approaches $R\ln 2$.

Cubic N₂O is ordered, however, in the sense that the molecular axes are aligned along the four cube diagonals.¹¹ This ordering is promoted by a sizeable electric quadrupole moment⁵ in the molecules, which causes them to assume approximate T formations. Arguing by analogy with the behavior of CO₂, which has the same molecular weight and a

similar electronic distribution and quadrupole moment, Kuchta and Etters¹³ calculated that N₂O should undergo a phase transition from the known cubic form at low pressure to an orthorhombic form at high pressure. Raman scattering measurements^{14,15} have already indicated a structure change of some sort in N₂O around 5 GPa at room temperature. We note that, unlike some of the other oxides of nitrogen, N₂O is stable under pressure up to at least 14 GPa.¹⁶

The present x-ray-diffraction study was carried out to explore the phase diagram of solid N₂O at high pressure and to compare the results with those for isoelectronic CO₂.

EXPERIMENT

Liquid N₂O with powdered NaF as a pressure indicator was loaded in a cylindrical hole in the center of a 2.5 mm diam Be gasket and clamped between tungsten carbide anvils. We used an indium-dam loading technique similar to that developed for diamond cells.¹⁷ The N₂O sample was condensed at 0.35 MPa where the liquid range extends from about 185 to 205 K.

Figure 1 shows the experimental setup. The lower anvil was constrained by tension rods while the upper one was driven by a hydraulic ram. A collimated beam of Cu K α x rays was directed radially through the Be gasket and sample, and the diffracted radiation was recorded on film in a 114.6 mm diam powder camera, as shown in Fig. 1.

Experiments were carried out both at room temperature and near 100 K. We cooled the sample by circulating liquid N₂ through channels in the platens supporting the carbide anvils. The temperature was measured and controlled by a copper-constantan thermocouple in contact with the edge of the Be gasket. In a separate experiment, the temperature difference between the center and edge of the gasket, when compressed between the anvils, was shown to be less than 1 K.

Cell pressures were deduced from x-ray-determined volumes of *in situ* powdered NaF. The P–V relation for NaF is

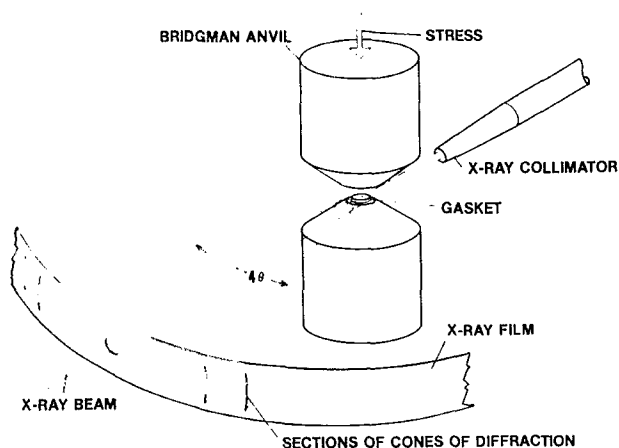


FIG. 1. Schematic diagram of the apparatus.

known from shock-wave and ultrasonic data.¹⁸ Relative volumes of NaF as a function of pressure at 298 K are tabulated in an earlier paper¹ in which we discuss the conversion of these pressures to lower temperature values. Also in Ref. 1 the NaF shock-wave pressure scale is compared with the ruby-fluorescence scale commonly used in diamond cell work, such as the Raman scattering measurements¹⁴ on N₂O. To obtain the cleanest diffraction patterns possible at 298 K, some experiments were carried out with no NaF in the cell. Pressures in these runs were calculated from fits of N₂O molar volumes obtained in the presence of NaF.

Five series of x-ray-diffraction patterns were taken of N₂O at high pressures. The first series failed because N₂O was not properly loaded into the gasket. To promote loading in the second series, we increased the size of the sample hole from a right cylinder of 250 μ m to one of 500 μ m. The N₂O was successfully loaded, but the large sample gave patterns that, although distinguishable, were too broad and diffuse for accurate measurement. The NaF that was mixed with the N₂O, however, did yield good diffraction patterns from which accurate pressures could be computed. This series of runs was used to determine the phase regions in N₂O within the range of the apparatus, up to 12 GPa at room temperature.

For the third series of experiments, we returned to the smaller 250 μ m sample size. Sixteen useful diffraction patterns were obtained at 298 K, and these x-ray films provide data for determining compression curves for N₂O. The fourth series of diffraction pictures was taken at various densities without a pressure indicator in the sample. These relatively clean films were used for structure determinations of N₂O. The fifth series was used to locate the phase boundary at low temperatures. Various pressures were set at 298 K after which the temperature was lowered and patterns were taken.

We observed x-ray powder diffraction patterns from two different structures for N₂O over the range 100 to 300 K and 2 to 12 GPa. The lower pressure form, which had been named¹⁴ N₂O-I and which we now designate α -N₂O, was

known⁶⁻¹¹ to have a cubic structure with effective space group Pa3. The new, higher pressure form, formerly called¹⁴ N₂O-II and here called β -N₂O, is an orthorhombic structure. In Table I we show the room-temperature diffraction pattern from run 3-6 for α -N₂O at 4.81 GPa. Table II shows the room-temperature pattern from run 4-11 for β -N₂O at a molar volume corresponding to a pressure of 5.81 GPa. In Table III we list the pressure, structure, lattice parameters, and molar volume for our observations on N₂O at 298 K.

DISCUSSION

α -N₂O structure

The space group of α -N₂O at low pressure is known from x-ray,⁶⁻⁹ electron,¹⁰ and neutron¹¹ diffraction studies to be Pa3. The four molecules in the unit cell are centered on lattice sites with each molecular axis aligned along a different cube diagonal. If the molecules were polarized with repeating head-to-tail orientation, the space group would be P2₁3. There is, however, evidence from thermodynamic¹² and neutron diffraction¹¹ studies that the head-to-tail arrangement is largely random, which would lead to a Pa3 space group.

In modeling α -N₂O, we treated the molecule as a rigid body with one N atom at the center and a composite atom consisting of $\frac{1}{2}$ N + $\frac{1}{2}$ O fixed on each end at a distance of 1.15 Å, the mean of the N-N and N-O values. This model approximates a random end-for-end arrangement of the N₂O molecules.

We used the ANIFAC program¹⁹ to calculate the intensities shown in Table I. Agreement with the rather crude intensities read from the x-ray films is satisfactory. The intensity residual

$$R_I = \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum |I_{\text{obs}}|}$$

is 20%, which corresponds to a residual in structure factor R_F of about 10%. Our observations in Tables I and III, al-

TABLE I. Observed and calculated x-ray powder pattern for α -N₂O at 4.81 GPa and 298 K. (Run 3-6).

<i>hkl</i>	<i>d</i> _{obs} (Å)	<i>a</i> ^a (Å)	<i>I</i> _{obs}	<i>I</i> _{calc} ^b
111	3.022	5.234	100	100.0
200	2.621	5.241	20	13.6
210	2.343	5.240	80	51.1
211	2.139	5.239	40	35.5
220	1.854	5.244	5	7.8
221	c	c	c	0.0
311	c	c	c	0.3
222	1.543	5.242	5	2.1
302	1.453	5.240	10	6.3
321	1.400	5.238	20	11.2

^a Average cell constant $\bar{a} = 5.240 \pm 0.002$ Å.

^b Calculated for Pa3 model described in text.

^c Possible reflection masked by strong line from Be gasket.

though not conclusive, are nevertheless consistent with a Pa3 space group for α -N₂O up to about 4.8 GPa where the α - β transition occurs at room temperature.

β -N₂O structure

Each x-ray photograph of β -N₂O exhibited a diffraction pattern that was clearly different from that for α -N₂O. We compared the β pattern with Hull-Davy charts and were able to narrow the possible structures to orthorhombic, in accord with the theoretical prediction of Etters and Kuchta.¹³ The diffraction lines of β -N₂O in Table II were indexed on the basis of an orthorhombic cell with $a = 4.954$ Å, $b = 4.497$ Å, and $c = 6.201$ Å. Systematic extinctions were consistent with space groups Cmca and Aba2. The molecular volume of β -N₂O under the experimental conditions was estimated to be 34.9 Å³ from an extrapolation of our α -N₂O x-ray volumes, neglecting any volume change on transition. This required that the orthorhombic unit cell contain four molecules.

We used Busing's²⁰ WMIN program to orient the N₂O molecules, the potential parameters of which were taken from Mirsky.²¹ Again, the molecule was treated as a rigid body with a random end-for-end arrangement modeled as described previously for α -N₂O. The molecule was centered at 0,0,0 with an arbitrary starting orientation in the bc plane

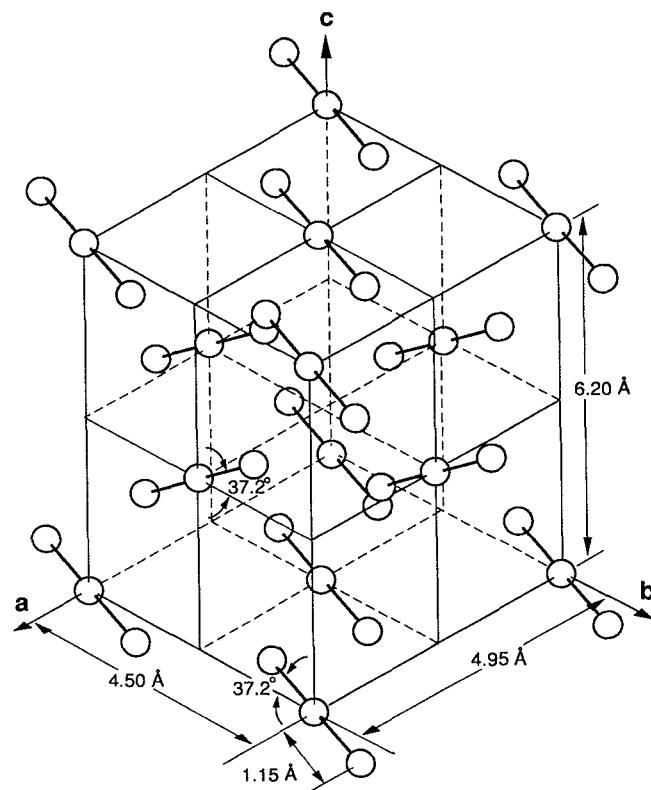


FIG. 2. Isometric projection showing structure of orthorhombic β -N₂O (Cmca) at 5.8 GPa and 298 K. Center atom, N; end atoms, N and O randomly arranged.

TABLE II. Observed and calculated x-ray powder pattern for β -N₂O at $V = 20.79$ cm³/mol^a and 298 K. (Run 4-11.)

hkl	d_{obs}^b (Å)	d_{calc}^c (Å)	I_{obs}^d	I_{calc}^e Model 1	I_{calc}^e Model 2
002	3.102	3.1000	30	24.6	2.6
111	2.935	2.9335	100	100.0	100.0
200	2.471	2.4770	40	65.9	42.2
112	2.267	2.2689	100	81.8	0.0
020	2.248	2.2485	10	3.3	29.7
021	2.114	2.1138	10	4.5	0.0
202	...	1.9351	(10)	8.8	1.1
022	e	1.8201	e	1.8	0.8
113	e	1.7559	e	2.8	5.0
220	...	1.6649	(10)	2.0	17.2
221	...	1.6079	(5)	2.8	0.0
004	...	1.5500	(5)	1.2	0.5
023	1.521	1.5216	5	1.9	0.0
311	1.504	1.5038	5	7.1	7.1
222	...	1.4667	(5)	1.4	0.6
114	...	1.4052	...	1.0	0.0
131	...	1.3978	...	0.2	5.0
312	1.387	1.3865	5	9.8	0.0
204	...	1.3140	...	1.1	0.5
132	...	1.3021	...	3.2	0.0
223	...	1.2965	...	1.8	0.0
024	...	1.2762	(5)	5.6	0.4

^a For this value of V , Eq. (7) gives $P = 5.81$ GPa.

^b Cell constants determined by least-squares fit are $a = 4.954$ Å, $b = 4.497$ Å, and $c = 6.201$ Å.

^c Intensities in parentheses are from photos of β -N₂O at other values of P and T .

^d Model 1 is for space group Cmca with N₂O molecule in bc plane tipped up 37.2° from ab plane. Model 2 is for space group Cmca with N₂O molecules parallel to c axis.

^e Possible reflection masked by strong line from Be gasket.

of space group Cmca and allowed to rotate. Using Busing's mode 3 (Rosenbrock Search),²⁰ we found an energy minimum when the three atoms in the molecule were positioned at (0, 0.204, 0.112), (0,0,0), and (0, -0.204, -0.112), with the molecular axis tipped at an angle of 37.2° to the b axis. The β -N₂O structure, shown in Fig. 2, has near interatomic distances of 2.74, 2.81, 3.03, and 3.13 Å and is our model 1.

Table II gives the observed x-ray intensities for β -N₂O and those calculated using the ANIFAC program.¹⁹ The intensity residual R_I for model 1 is 23%, which corresponds to $R_F \approx 12\%$. We consider this to be acceptable in view of the necessarily rough experimental intensities. Also shown in Table II are computed intensities for a model 2 in which all four of the molecules are parallel to the c axis. The agreement is poor and gives several instances where $I_{\text{calc}} = 0$ for reflections that were clearly observed. Therefore, we dismiss model 2. Additional calculations using WMIN for space group Aba2 gave a solution identical to that for the centrosymmetric space group Cmca.

We calculated electron density contours for an isolated N₂O molecule using a published²² wave function. The contours out to 0.002 e^-/bohr^3 , which encompass almost all of the electronic charge, are reproduced in Fig. 3. The 0.002 contour of a free molecule has been shown²³ to approximate the size and shape of molecules packed in van der Waals lattices at low pressure. Packing analyses were useful in ex-

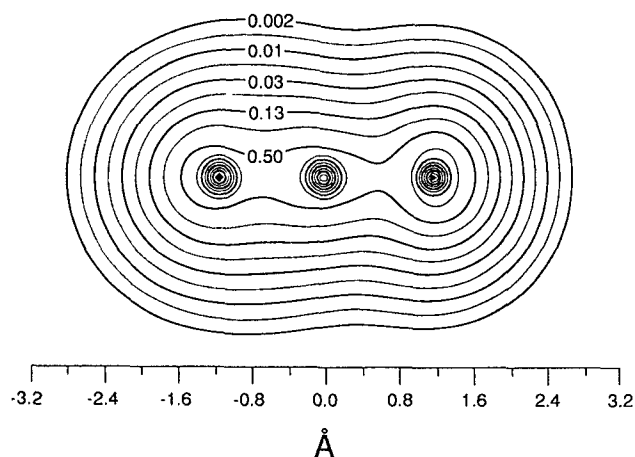


FIG. 3. Electron density contours in the N-N-O molecule computed using the wave function from Ref. 22. The electron density (ρ) is given in e^-/bohr^3 ($= 6.749 e^-/\text{\AA}^3$). Plotted is $\log_{10}(\rho)$, with a spacing of 0.3 between contour lines. The outermost contour corresponds to $\log_{10}(\rho) = -2.7$, or $\rho = 0.002$.

plaining phase transitions that occur at higher pressures.^{24,25} In Fig. 4 we show how the molecules on the 200 face must be packed in β -N₂O near 6 GPa and room temperature. An undistorted free molecule would touch on about the 0.006 or 0.01 contour.

Phase diagram

In several of the x-ray photographs for N₂O, diffraction patterns showed coexisting α and β phases. Assuming that the corresponding P and T values lie close to the α - β transition line, we have plotted these points in Fig. 5(a) and drawn

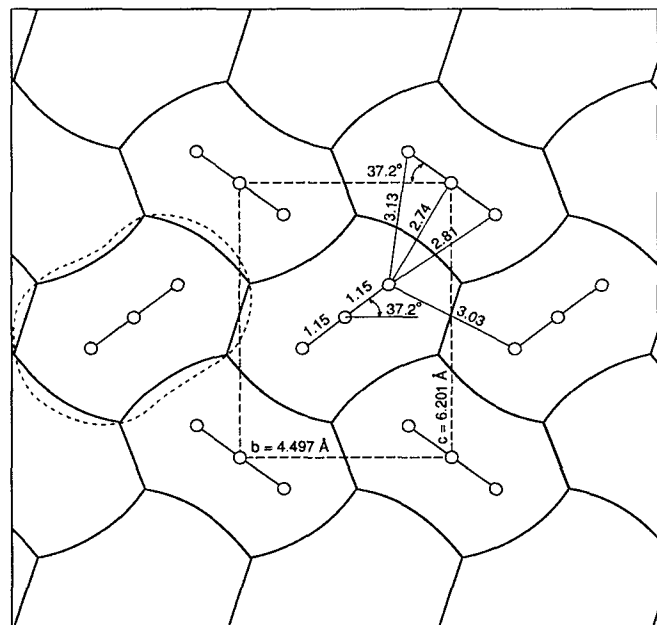


FIG. 4. Packing of molecules on bc face of β -N₂O at 5.8 GPa and 298 K showing distortion of free molecule from Fig. 3.

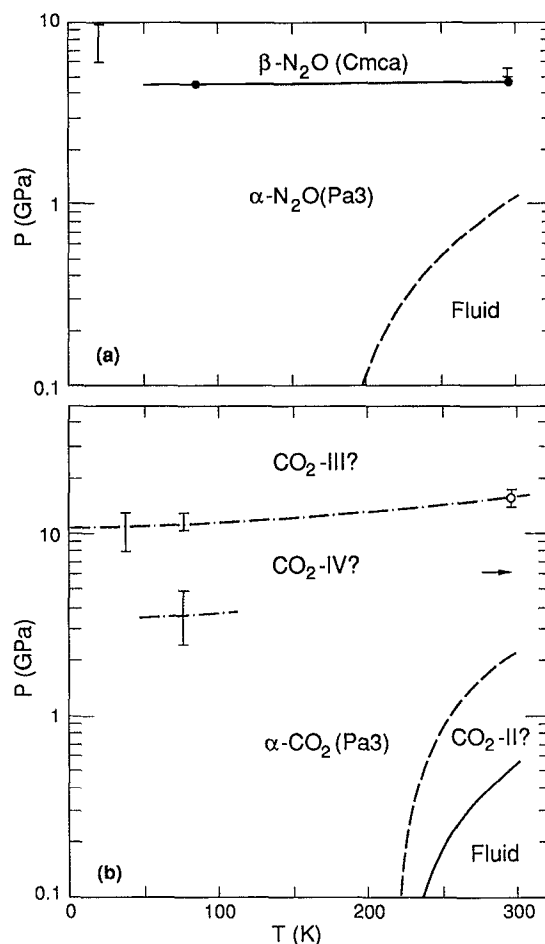


FIG. 5. Diagrams showing fluid and solid phases with space groups in parentheses. (a) N₂O: closed circle, present measurement; bar, Ref. 14; dashed line, Eq. (1) melting curve extrapolated from data of Ref. 26 as discussed in text. (b) CO₂: solid line, melting curve Refs. 27–29; dashed line, proposed phase boundary Ref. 37; open circle, transition Ref. 33; bar, Ref. 39 with phase boundary shown as dash-dot line; cross-hatch zone, provisional phase boundary Ref. 39; arrow, transition observed in Ref. 28.

a solid line through them to represent the new phase boundary. It appears that the transition pressure is almost independent of temperature.

The α -solid/fluid transition line for N₂O at high pressure was calculated from the melting point data of Clusius *et al.*,²⁶ measured to 0.025 GPa and expressed by them as a quadratic in P . We refitted their data within their experimental uncertainty to a Simon-type equation more suitable for extrapolation and obtained

$$P = -0.40521 + 0.35674 \times 10^{-6} T^{2.6786} \text{ GPa}, \quad (1)$$

which is shown as the dashed curve in Fig. 5(a). The room-temperature freezing pressure is estimated to be 1.1 GPa, but because of the gross extrapolation, this value should be used as a guide only.

In Fig. 5(b) we have plotted the phase diagram of CO₂ on a common temperature scale for comparison with that of N₂O. The fluid boundary line has been determined up to about 0.4 GPa by Tamman,²⁷ 1.2 GPa by Bridgman,²⁸ and 0.28 GPa by Michels *et al.*,²⁹ all in fair agreement.

There is, however, considerable uncertainty about the solid phases of CO₂. In chronological order, it was reported that low-pressure carbon dioxide solidifies into a cubic structure³⁰ with space group Pa3, which we here call α -CO₂ and which was shown by Raman spectra^{31,32} to exist down to at least 15 K. Hanson and Jones³³ made infrared and Raman measurements on CO₂ at room temperature from the freezing pressure near 0.5 GPa up to 12 GPa, with no indication of a phase change. Using powder x-ray-diffraction at 296 K, Olinger³⁴ also found no structure change in CO₂ from 1 to 10 GPa. The solid remained cubic Pa3. Similarly, Krupskii *et al.*³⁵ found no change from Pa3 in their x-ray patterns down to 6 K at low pressure.

Liu,³⁶ however, reported that his optical and powder x-ray studies at ambient temperature showed a new, and still-undetermined, CO₂-II structure to be stable from the freezing point at 0.5 GPa up to 2.3 GPa and gave the tentative phase boundary shown as the dashed curve in Fig. 5(b). He subsequently reported³⁷ powder x-ray work that indicated CO₂ again takes on the Pa3 form from 2.3 to 50 GPa.

Hanson³⁸ found a dramatic change in the low-frequency Raman spectrum of solid CO₂, which occurs in the region between 15 and 18 GPa at room temperature, and which he interpreted as a solid transition. Recently Olijnyk *et al.*,³⁹

using Raman scattering, also found evidence that a structure change takes place in CO₂ between about 11 and 18 GPa over the temperature range 40–300 K. Moreover, from similarities in spectra, they proposed that the CO₂-III high-pressure phase may be identical to the high-pressure β phase of N₂O, which forms at the much lower pressure of about 5 GPa and which we report here to be orthorhombic (Cmca). If a structure change to Cmca occurs in room-temperature CO₂ near 15 GPa, however, it should have been detected in Liu's³⁷ work. Evidence for a CO₂-IV phase was also reported by Olijnyk *et al.*³⁹

Some of the uncertainty in the CO₂ measurements may have resulted from contaminants in the commercial "dry ice" samples or from air, H₂O, and N₂ introduced during loading, although recent x-ray studies⁴⁰ on pure CO₂, loaded as a liquid by indium-dam technique,¹⁷ have confirmed earlier results³⁴ using "dry ice." Also, solid CO₂ is known to be subject to large distortions caused by uniaxial stress. Clearly, more experiments are needed to establish unambiguously the phase diagram of solid CO₂.

Molar volumes

Molar volumes of N₂O at 298 K from Table III are plotted in Fig. 6 as solid symbols. The volume data can be

TABLE III. Summary of N₂O x-ray data^a at 298 K.

Run	a_{NaF} (Å)	P (GPa)	Phase	a (Å)	b (Å)	c (Å)	V (cm ³ /mol)
3-2	4.568 (0.002)	2.24 (0.05)	α	5.425 (0.006)			24.03 (0.08)
3-3	4.550 (0.001)	2.94 (0.03)	α	5.368 (0.002)			23.28 (0.03)
3-4	4.535 (0.001)	3.57 (0.04)	α	5.315 (0.001)			22.60 (0.01)
3-5	4.521 (0.002)	4.16 (0.08)	α	5.275 (0.004)			22.09 (0.05)
3-6	4.507 (0.002)	4.81 (0.08)	α	5.240 (0.002)			21.66 (0.03)
3-7	4.492 (0.001)	5.48 (0.02)	β	4.965 (0.008)	4.496 (0.007)	6.227 (0.010)	20.92 (0.10)
3-8	4.486 (0.003)	5.82 (0.10)	β	4.950 (0.006)	4.486 (0.005)	6.234 (0.004)	20.83 (0.06)
3-9	4.473 (0.001)	6.48 (0.02)	β	4.919 (0.003)	4.459 (0.003)	6.196 (0.005)	20.45 (0.04)
3-10	4.461 (0.003)	7.10 (0.10)	β	4.897 (0.002)	4.438 (0.001)	6.182 (0.002)	20.22 (0.02)
3-11	4.452 (0.004)	7.59 (0.19)	β	4.851 (0.004)	4.448 (0.011)	6.151 (0.007)	19.97 (0.09)
3-12	4.423 (0.006)	9.27 (0.27)	β	4.787 (0.008)	4.422 (0.022)	6.127 (0.013)	19.52 (0.17)
3-13	4.421 (0.001)	9.34 (0.07)	β	4.771 (0.011)	4.416 (0.028)	6.120 (0.017)	19.41 (0.22)
3-14	4.406 (0.002)	10.30 (0.10)	β	4.743 (0.018)	4.399 (0.048)	6.108 (0.029)	19.18 (0.37)
3-15	4.403 (0.001)	10.46 (0.05)	β	4.729 (0.016)	4.390 (0.042)	6.101 (0.025)	19.06 (0.33)
3-16	4.392 (0.001)	11.21 (0.03)	β	4.722 (0.013)	4.388 (0.034)	6.062 (0.020)	18.90 (0.26)
3-17	4.386 (0.003)	11.61 (0.20)	β	4.712 (0.030)	4.399 (0.078)	6.061 (0.046)	18.91 (0.60)

^aStandard deviations shown in parentheses.

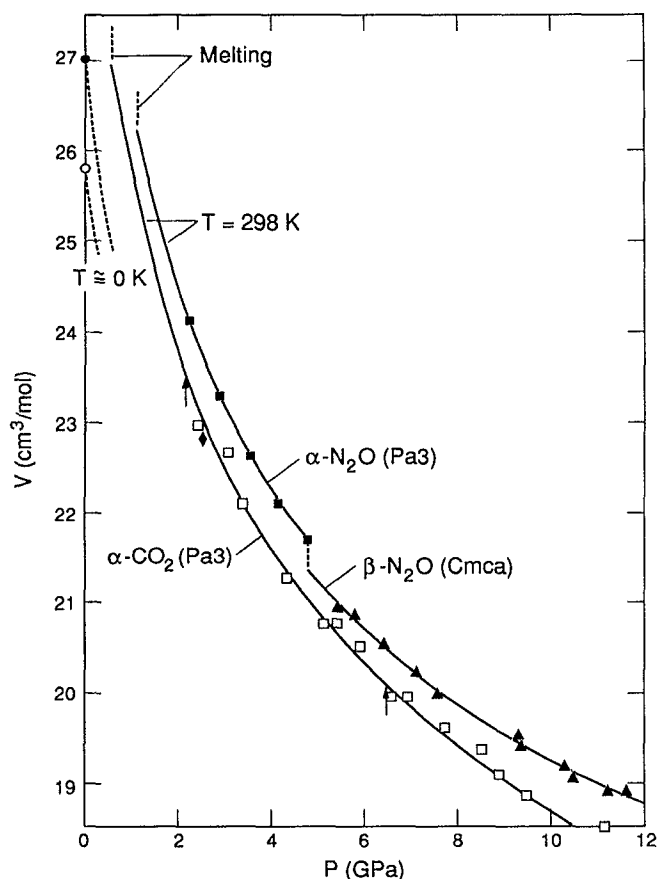


FIG. 6. Volume-pressure isotherms of N₂O (closed symbol) and CO₂ (open symbol). Closed square, α -N₂O (Pa3) present measurement with solid line Eq. (6); solid triangle, β -N₂O (Cmca) present measurement with solid line Eq. (7); solid diamond, theoretical prediction at 0 K Ref. 13; open square, α -CO₂ Ref. 37 with solid line Eq. (6) Ref. 34; solid circle, α -N₂O Ref. 9; open circle, α -CO₂ Ref. 10; arrow, transition reported in Refs. 28 and 36. All pressures have been converted to NaF scale.

represented by a velocity-plane equation of state³⁴ in terms of the shock velocity, ψ_s , and particle velocity, ψ_p , where

$$\psi_s = [PV_0/(1 - V/V_0)]^{1/2}, \quad (2)$$

$$\psi_p = [PV_0(1 - V/V_0)]^{1/2}, \quad (3)$$

$$P = \psi_s \psi_p / V_0, \quad (4)$$

and

$$V = V_0(\psi_s - \psi_p)/\psi_s. \quad (5)$$

The relationship between ψ_s and ψ_p is linear for solid N₂O in our pressure regime. A linear least-squares fit to the volume data for α -N₂O from Table III gives

$$\psi_s = 2.080 + 1.563\psi_p \text{ km/s},$$

and

$$V_0 = 0.6655 \text{ cm}^3/\text{g}, \quad (6)$$

where V_0 is now a fitted, hypothetical value of V at $P = 0$.

A similar fit of β -N₂O volumes from Table III over the range 5.5–11.6 GPa at room temperature gives

$$\psi_s = 1.686 + 1.669\psi_p \text{ km/s},$$

and

$$V_0 = 0.6900 \text{ cm}^3/\text{g}. \quad (7)$$

By comparing Eq. (6) with Eq. (7) at their disjoints corresponding to the α - β transition, we estimate that the volume change on transition, ΔV_{tr} , is about 1%. Using an estimated slope $(dP/dT)_{tr}$ of about 0.01 GPa/K for the transition line in Fig. 5(a), we compute an entropy change on transition $\Delta S_{tr} = \Delta V_{tr} (dP/dT)_{tr}$ of only ~ 0.5 cal/mol K.

Literature values of molar volumes for CO₂ are also shown in Fig. 6. The x-ray measurements made in a diamond cell by Liu,³⁷ shown as open squares, have been raised slightly in pressure to agree with the NaF scale. The maximum shift is about 3% at 10 GPa.¹ We see that there is excellent agreement with the earlier x-ray data of Olinger³⁴ shown as the solid line. This line also represents theoretical calculations of CO₂ volumes by LeSar and Gordon⁴¹ with a deviation of only 0.5%. There are, however, no published volume data that confirm the crystallographic transitions claimed for solid CO₂, and indicated by arrows in Fig. 6.

Theoretical predictions

From lattice energy calculations at 0 K, Etters and Kuchta¹³ predicted a pressure-induced transition at 2.56 GPa from the known cubic α -N₂O (Pa3) to a new orthorhombic structure with space group Cmca. The unit cell dimensions were calculated to be $a = 5.1$ Å, $b = 4.5$ Å, and $c = 6.6$ Å with the four molecules lying parallel to the bc plane and tipped up from the b axis at an angle $\Theta = 45$ – 50° . The computed molar volume, $22.8 \text{ cm}^3/\text{mol}$, is plotted as the closed diamond in Fig. 6. Our measurements at room temperature are in excellent agreement with theory, giving the predicted space group Cmca with $a = 5.0$ Å, $b = 4.5$ Å, $c = 6.2$ Å, $\Theta = 37.2^\circ$, and $V = 21.4 \text{ cm}^3/\text{mol}$. Only the computed transition pressure appears to be in serious conflict with experiment. As in the case¹ of N₂ and CO, it is quite encouraging that theoretical calculations yield such accurate predictions.

It is of interest to compare the crystal structures of CO₂ and N₂O to those of another linear molecule, C₂H₂, which has a transition from the Pa3 structure to Cmca as the temperature is lowered to below 133 K at zero pressure.⁴² Recent calculations⁴³ found that the energies of these structures are almost identical at zero pressure and temperature, but that pressure stabilizes Cmca relative to Pa3. It was also suggested that the phase line should be quite shallow with temperature and that only a modest pressure would be necessary to transform Pa3 to Cmca at room temperature. Both predictions were later verified experimentally,⁴⁴ where the transition was observed at about 0.7 GPa. The calculations indicated that even though it has long been suggested that the Pa3 structure is favored for molecules with large quadrupole moments, the total electrostatic energies for the two crystal structures are almost identical. Indeed, it was found that the Cmca structure is actually stabilized by the long-range van der Waals energy. Cmca is favored at higher pressure largely because it has a smaller volume, which minimizes the PV term in the Gibbs free energy. Thus, given the similarities between the molecules (relatively long, linear molecules with large electrostatic moments), it should, per-

haps, not surprise us that both N₂O and CO₂ seem to follow the same pattern of Pa3 at low pressures and Cmca at high pressures with a very flat transition line.

In a companion paper immediately following the present publication, Kuchta and Etters¹³ have refined their theoretical calculations of the structures and transitions of N₂O. The agreement with experiment is even more impressive.

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