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Room-Temperature Structure of Carbon Monoxide at 2·7 and 3·6 GPa

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Abstract. A single crystal of CO was grown at room temperature in a high-pressure Merrill–Bassett diamond cell and examined by X-ray diffraction at 2·7 and 3·6 GPa. At 4·2 GPa the sample appeared to undergo a photochemical change induced by the weak laser light used to make ruby fluorescence pressure measurements. The unit cell is hexagonal, space group $P6_3/mmc$, with two molecules per unit cell, which is the same as that of β-CO near the triple point. At $P = 2{\cdot}7$ GPa the lattice constants are $a = 3{\cdot}615$ (1) and $c = 5{\cdot}880$ (1) Å, and at 3·6 GPa they are $a = 3{\cdot}532$ (1) and $c = 5{\cdot}744$ (2) Å, giving molar volumes very near to those for β-N_2 under similar conditions. The final R_w, refined from ten observations, is 0·103 for a model with molecules tilted 49° from the *c* axis, statistically disordered, and randomly polarized. Calculations using a Gordon–Kim electron-gas model show that the $P6_3/mmc$ structure with randomly polarized CO molecules should have a minimum energy at a tilt angle of 50°, while polarized molecules give 48°. The melting pressure of CO at room temperature is about 2·6 GPa and is considerably lower than published measurements would indicate.

Introduction. Recent experimental and theoretical studies of molecular crystals have been aimed at a detailed understanding of intermolecular potentials, which determine the way physical properties vary with pressure and temperature. Using improved models and more powerful computing techniques, we can now predict with some success the crystal structures and phase diagrams of a few simple molecules (LeSar & Gordon, 1982).

N_2 and CO constitute a useful pair of molecules for separate study because they show many striking similarities, especially at low pressure (Raich & Mills, 1971). The two molecules are isoelectronic, have the same molecular size and weight, and condense into liquids with almost identical molar volumes. Liquid CO and N_2 freeze at triple points of 68·15 and 63·14 K, respectively, giving a disordered hexagonal solid, the β phase, which on further cooling transforms into an ordered cubic structure, the α phase. The crystallographic transition occurs at 61·6 K for CO and 35·6 K for N_2 and is driven primarily by electric quadrupole–quadrupole interactions.

For many years a controversy brewed over whether the molecules in α-N_2 are centrosymmetric in space group $Pa3$ (Ruhemann, 1932; Bolz, Boyd, Mauer & Peiser, 1959; Hörl & Marton, 1961; Schuch & Mills, 1970; Venables, 1970; Kjems & Dolling, 1975) or whether they are slightly shifted along the cube diagonals giving space group $P2_13$ (Vegard, 1929; Jordan, Smith, Streib & Lipscomb, 1964; Brookeman, McEnnan & Scott, 1971; LaPlaca & Hamilton, 1972; Wachtel, 1972). A definitive electron-diffraction study, however, by Venables & English (1974) shows that twinning of the (111) planes in the $Pa3$ structure can explain much of the evidence that led previously to the assignment of space group $P2_13$.

There is also dispute about the exact nature of the disorder in β-N_2. Streib, Jordan & Lipscomb (1962) reported the space group to be $P6_3/mmc$ with molecules precessing around the *c* axis at an angle of about 55°, whereas Press & Hüller (1978) favor a spherically disordered model from a careful reanalysis of X-ray, NQR, and theoretical work.

The structure determinations of α-CO are likewise conflicting (Lipscomb, 1964). From X-ray measurements, Krupskii, Prokhvatilov, Erenburg & Yantsevich (1973) found the $Pa3$ space group, while Vegard (1930)

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and Anderson, Sun & Donkersloot (1970) reported $P2_13$. The latter structure is expected by those who argue that CO molecules lack inversion symmetry and should crystallize in a noncentrosymmetric structure. Hall & James (1976), however, calculated that any distortion of the CO molecules from the $Pa3$ arrangement should be quite small. The nature of the disorder in hexagonal β-CO is unknown (Vegard, 1934).

In contrast to nitrogen, carbon monoxide is heteronuclear. The molecules in solid CO exhibit end-for-end disorder which is largely frozen-in during solidification. The dipole moment in CO is too weak to orient the molecules at low temperature where kT is comparable to the dipolar energy, and, consequently, solid CO has a residual entropy of about $R\ln 2$ at 0 K (Clayton & Giauque, 1932).

The differences between CO and N_2 become more pronounced at higher pressure where the repulsive part of the intermolecular potential is being sampled. Ordered cubic α-N_2 ($Pa3$) transforms into an ordered tetragonal γ-N_2 ($P4_2/mnm$) structure at temperatures between 0 and 40 K and pressures above about 0·35 GPa (Mills & Schuch, 1969; Schuch & Mills, 1970), whereas no such transition has been observed in solid carbon monoxide up to 0·45 GPa (Stevenson, 1957; Schuch & Mills, 1970). The large quadrupole moment in CO, $-8{\cdot}3 \times 10^{-40}$ C m^2 compared to $-5{\cdot}0 \times 10^{-40}$ C m^2 for N_2, has been shown by Felsteiner & Litvin (1971) to be incompatible with a tetragonal space group, although Raich & Mills (1971) predict that high pressures may override this effect and promote an α-CO to γ-CO transition in the vicinity of 4·8 GPa.

A further difference appears in work by Fukushima, Gibson & Scott (1977), showing that the melting pressure of CO rises with temperature as $T^{2{\cdot}695}$, which is much faster than the $T^{1{\cdot}790}$ dependence that Mills, Liebenberg & Bronson (1975) observed in N_2. In the present work, however, we find that the melting pressures of CO and N_2 are quite similar near room temperature. Our study also shows that chemical differences between CO and N_2 become manifest at about 4·2 GPa where CO apparently undergoes a photochemical reaction.

We are extending our previous experiments on nitrogen (Mills & Schuch, 1969; Schuch & Mills, 1970; Mills *et al.*, 1975; Raich & Mills, 1971; Schiferl, Cromer & Mills, 1978; Schwalbe, Schiferl, Mills, Jones, Ekberg, Cromer, LeSar & Shaner, 1980; LeSar, Ekberg, Jones, Mills, Schwalbe & Schiferl, 1979; Cromer, Mills, Schiferl & Schwalbe, 1981) to carbon monoxide, with the hope of uncovering subtle variations in the molecular interactions that cause CO to behave differently from N_2. Reported here are room-temperature X-ray diffraction measurements on a single crystal of CO in a diamond cell at 2·7 and 3·6 GPa. The structure is hexagonal ($P6_3/mmc$) and is the same as that reported for β-CO at 61·5 K under its own vapor pressure (Vegard, 1934).

Experimental. A Merrill–Bassett diamond-anvil cell (Merrill & Bassett, 1974), modified to utilize stronger beryllium pieces (Schiferl, 1977) and to provide uniform X-ray absorption and better optical access (Keller & Holzapfel, 1977), was loaded by condensing high-purity carbon-monoxide gas into it, using the indium-dam technique (Liebenberg, 1979; Mills, Liebenberg, Bronson & Schmidt, 1980). Mass spectroscopic analysis showed 0·15% CH_4, 0·04% CO_2, and 0·02% O_2 as the only measurable impurities. Pressure was measured with the ruby fluorescence method, assuming the R_1 lineshift to be given by the linear relation $d\lambda/dP =$ 0·365 nm GPa^{-1} (Forman, Piermarini, Barnett & Block, 1972; Barnett, Block & Piermarini, 1973).

A single crystal of CO formed as soon as the sample was taken to 2·59 GPa at 299 K. During the course of our first X-ray measurements, the pressure rose to 2·85 GPa and the room temperature fluctuated by several degrees. The sample conditions under which this X-ray experiment was made were 2·73 ± 0·13 GPa and 299 ± 2 K. A second X-ray study was carried out on the same crystal at 3·60 ± 0·06 GPa and 299 ± 2 K. Precession photographs showed the structure at both pressures to be similar to that of β-CO and β-N_2 at zero pressure. The lattice constants of the hexagonal unit cell, measured on a Picker diffractometer, were determined to be $a = 3{\cdot}615$ (1) and $c = 5{\cdot}880$ (1) Å at 2·73 GPa, and $a = 3{\cdot}532$ (1) and $c = 5{\cdot}744$ (2) Å at 3·60 GPa, from a least-squares refinement of three reflections, each measured by the eight-position Hamilton (1974) technique, and each with $13 < 2\theta < 15°$. We assumed the value $\lambda = 0{\cdot}7093$ Å for the wavelength of Mo $K\alpha_1$ radiation in calculating the lattice constants. It would have been desirable to use more reflections and to use reflections with higher 2θ values, but an unlucky orientation of the crystal in the diamond cell and a high Debye–Waller factor precluded this.

We made intensity measurements only on the lower-pressure CO crystal. An automated Picker diffractometer was used and the data were processed and weights determined in the manner described by Cromer & Larson (1977). All reflections not shadowed by the pressure cell were measured out to $2\theta = 38°$ with graphite-monochromated Mo $K\alpha_1$ radiation. The structure was assumed to be that of β-CO which has space group $P6_3/mmc$, with the molecules randomly polarized. However, if the molecules are polarized with the carbon atoms in, say, the $+z$ direction, the space group is $P6_3mc$. There were 53 nonspace-group($P6_3mc$)-extinguished reflections which were reduced to 15 nonequivalent reflections. Of these, ten reflections were observed according to the criterion $I \geq 3\sigma(I)$. Absorption corrections were judged to be unnecessary. A comparison of equivalent reflections gave $R_F = 0{\cdot}045$ (Cromer & Larson, 1977).

The sample remained clear and colorless throughout the X-ray measurements. After pressure on the CO crystal had been increased to 4·2 GPa, however, the sample immediately turned yellow brown when irradiated by 10 mW incident power from the 514·5 nm line of an argon laser. This behavior almost certainly indicates a photochemical change, and does not seem to be caused by the focused laser beam heating the sample. A second CO sample at 4·2 GPa, after being heated in boiling water for half an hour, remained clear and colorless, but also changed color when exposed to the laser beam.

With the assignment of two CO molecules to the hexagonal unit cell, we calculate a 299 K molar volume V of 20·05 cm^3 at 2·7 GPa and 18·69 cm^3 at 3·6 GPa. There are no published values of V for comparison, but Stevenson (1957) measured the compressibility of β-CO up to 1·0 GPa at 65 K. Taking 30·15 cm^3 for the molar volume of β-CO at $P = 0$ GPa and $T = 65$ K (Fukushima *et al.*, 1977), we were able to represent Stevenson's data within experimental error by

$$V(T = 65\ \mathrm{K}) = 23{\cdot}09\,(P + 0{\cdot}24)^{-0{\cdot}1576}, \qquad (1)$$

where $V(T = 65\ \mathrm{K})$ is the molar volume in cm^3 of β-CO along the 65 K isotherm and P is the pressure in GPa. Extrapolated molar volumes from (1) are $V(T = 65\ \mathrm{K}) = 19{\cdot}48$ cm^3 at $P = 2{\cdot}7$ GPa and $V(T = 65\ \mathrm{K}) = 18{\cdot}68$ cm^3 at $P = 3{\cdot}6$ GPa. With the assumption that the average thermal expansion coefficient for β-CO is similar to the value $3 \times 10^{-4}\ \mathrm{K}^{-1}$ for β-N_2 (Mills *et al.*, 1975), the 2·7 and 3·6 GPa extrapolated molar volumes of CO become 20·9 and 20·1 cm^3, respectively, at $T = 299$ K. These very rough values deviate by only a few percent from the accurate volumes computed above using the X-ray cell constants, which shows that there are, indeed, two molecules per unit cell.

We performed least-squares structure refinements on β-CO using all of the realistic models for isostructural β-N_2 suggested by Streib *et al.* (1962). The refinements were based on F. Because CO is polar, we also performed several refinements assuming the molecules were polarized. The ratio of maximum least-squares shift to error for all models was less than 0·1. The following models were tested:

1. Statistically disordered molecules tilted from the c axis with no polarization (carbon atoms randomly up or down). The molecules are centered at the $2(d)$ positions $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}; \frac{2}{3}, \frac{1}{3}, \frac{1}{4}$. They are probably not rotating, but exhibit a static disorder that can be described by placing $\frac{1}{12}$ carbon atom and $\frac{1}{12}$ oxygen atom at the same site $24(l)$ of space group $P6_3/mmc$. Refinements were performed for tilt angles of 45, 46, 47, 48, 49 (best), and 50°.

2. Statistically disordered molecules tilted from the c axis, but polarized with the carbon atoms in the up direction. Except for polarization, this model is similar to model 1. The static disorder is described by placing $\frac{1}{6}$ carbon atom and $\frac{1}{6}$ oxygen atom at separate sites $12(d)$ of space group $P6_3mc$. Refinements were performed for tilt angles of 43, 44 (best), 45, 46, 47, 48, 49, and 50°.

3. Spherically disordered molecules centered on sites $2(d)$ of space group $P6_3/mmc$. The scattering factor for a spherically disordered CO molecule is given in Table 1.

4. C—O axis parallel to the c axis with no molecular polarization (carbon atoms randomly up or down). This is described by placing $\frac{1}{2}$ carbon atom and $\frac{1}{2}$ oxygen atom at the same site $4(f)$ of space group $P6_3/mmc$.

In all cases the internuclear distance was fixed at the gas-phase value of 1·10 Å (Sutton, 1958). The *xyz* values for models 1 and 2 were chosen to produce equally spaced points about the $\bar{6}$ axis. The small number of reflections coupled with uncertainties due to the large thermal motion (Busing & Levy, 1964) preclude an independent determination of the C—O bond length.

For models 1, 3, and 4 there are two parameters to refine, a scale factor and isotropic temperature factor B. Besides the scale factor, model 2 requires the refinement of separate temperature factors B_C and B_O for the carbon and oxygen atoms, respectively.

In Table 2 the observed structure factors are compared with values calculated for each of the models described above. For the first two models only the results for tilt angles yielding the respective minimum values of R_w are presented. Complete results for R_w as a function of tilt angle are: 0·130 (45°), 0·118 (46°), 0·109 (47°), 0·104 (48°), 0·103 (49°), 0·106 (50°) for model 1; and 0·098 (43°), 0·097 (44°), 0·097 (45°), 0·098 (46°), 0·099 (47°), 0·102 (48°), 0·103 (49°), 0·111 (50°) for model 2.

It is clear from Table 2 that models 1 and 2 provide a better fit to the data than models 3 or 4. The Hamilton (1965) ratio test indicates that model 2 with three parameters is not significantly better than model 1 with only two parameters.

Discussion. We find that the structure of CO at 2·7 GPa and 299 K can most simply be described by model 1 in which the molecular axis is tilted at an angle of 49° from the c axis. The high degree of disorder makes it very unlikely that the molecules are polarized as described by model 2. The molecules probably do not precess, because the potential-energy barriers for even hindered rotation are too high. Instead, the CO molecules must be statistically disordered.

It is interesting that in CO at 2·7 GPa and 299 K the 'tilted-molecule' model is clearly preferable to one with spherically disordered molecules, while in presumably isostructural N_2 at 50 K and vapor pressure, it is

Table 1. *Scattering factor f for a freely rotating* CO *molecule*

Carbon and oxygen scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculation for spherical molecules was done according to James (1948). Coefficients to fit f for $(\sin\theta)/\lambda \le 0.46$ Å^{-1} are $a_1 = 106.471$, $b_1 = -0.0269019$, $a_2 = 7.50325$, $b_2 = 7.46640$, $a_3 = 7.20349$, $b_3 = 22.5887$, $a_4 = 1.55246$, $b_4 = 52.0275$, $c = -108.732$.

$(\sin\theta)/\lambda$ (Å^{-1})	f	$(\sin\theta)/\lambda$ (Å^{-1})	f	$(\sin\theta)/\lambda$ (Å^{-1})	f
0·00	14·00	0·11	10·94	0·26	4·07
0·01	13·97	0·12	10·47	0·28	3·39
0·02	13·88	0·13	9·96	0·30	2·79
0·03	13·73	0·14	9·46	0·32	2·25
0·04	13·53	0·15	8·96	0·34	1·77
0·05	13·28	0·16	8·46	0·36	1·35
0·06	12·98	0·17	7·96	0·38	0·98
0·07	12·64	0·18	7·48	0·40	0·66
0·08	12·26	0·20	6·53	0·42	0·39
0·09	11·84	0·22	5·64	0·44	0·15
0·10	11·40	0·24	4·82	0·46	−0·05

Table 2. *Observed and calculated structure factors* (× 10) *for* CO *at* 2·7 GPa *and* 299 K

h	k	l	F_o*	F_c^a†	F_c^b	F_c^c	F_c^d
1	0	0	75	74	72	70	72
0	0	2	122	120	108	129	51
1	0	1	99	105	100	101	87
1	0	2	26	34	31	34	14
1	1	0	49	46	44	40	47
1	0	3	22	21	20	25	6
2	0	0	17	13	12	11	14
1	1	2	19	24	21	20	10
2	0	1	14	19	18	15	18
2	0	2	9	7	6	5	3
1	0	4	<5	1	6	4	5
1	2	0	<6	2	2	1	3
1	2	1	<5	2	3	1	4
1	1	4	<10	0	5	1	4
1	2	2	<8	1	1	0	1
Tilt angle (°)				49	44	—	0
x				0·2185	0·2276	$\frac{1}{3}$	$\frac{1}{3}$
y				0·5518	0·5610	$\frac{2}{3}$	$\frac{2}{3}$
z				0·8114	0·6827	$\frac{3}{4}$	0·8435
B(Å^2)				7 (1)	—	7 (2)	14 (5)
B_{C}(Å^2)				—	11 (3)	—	—
B_{O}(Å^2)				—	8 (1)	—	—
R_w				0·103	0·097	0·145	0·382
R				0·084	0·089	0·101	0·292
Goodness of fit				6·9	7·0	9·8	25·8

* The listed F_o values are scaled to fit model 1. Other models had slightly different scale factors.

† (*a*),(*b*),(*c*),(*d*) Models 1, 2, 3, 4, respectively, are described in the text.

difficult to distinguish between the two models. It would be informative to see if N_2 under conditions similar to those of our CO sample also favors a 'tilted-molecule' model. Unfortunately, the published intensity data for N_2 at 2·5 GPa and 296 K (Schiferl, Cromer & Mills, 1978) are not as accurate as the present CO data. One might argue that if the CO molecules show a preference for orientation along the c axis, the c/a ratio would tend to rise above the ideal value 1·633 for closest packing of hard spheres. The present results, however, give a slightly smaller ratio, namely 1·626, at both pressures.

The structural properties of CO were studied within the framework of a recent theory by LeSar & Gordon (1982). The method is based on the Gordon & Kim (1972) electron-gas model, and requires only the molecular electronic density and parameters for the pair dispersion interactions. We calculated the electron density from a published wavefunction (Huo, 1965) and fit it to spherical functions located at seven centers along the C—O bond. The nuclear charges at each center were varied to reproduce the CO moments which had been calculated by Huo (1965), using an experimental value of the dipole (Burrus, 1958, 1959). With the anisotropy coefficient $\kappa = 0.0905$ (Ron & Schnepp, 1967), the dispersion coefficient is $C_6 = 88.4$ atomic units (Parker & Pack, 1976).

Calculations were performed for the hexagonal $P6_3/mmc$ structure to determine the optimal angle that the molecular CO axis makes with the crystal c axis. We fixed the lattice parameters to the present 299 K results at 2·7 GPa. The components of the bond orientation vectors in the *ab* plane were fixed in the hexagonal directions, with the relative orientations of the two molecules in the unit cell chosen to minimize the energy. The angle of tilt was then varied to give a final minimum energy. For a non-polarized model the best angle is 48° and for a polarized model it is 50°, bracketing our experimental value of 49°.

The melting curve of carbon monoxide has been measured to 0·175 GPa by Fukushima *et al.* (1977), using changes in the nuclear spin–spin relaxation time T_2 of ^{13}C as an indicator of the liquid–solid transition. They were able to express the melting pressure P_m as a function of temperature T over the range $0 < P_m <$ 0·175 GPa and $68 < T < 95$ K by a Simon-type melting equation (Simon & Glatzel, 1929). Extrapolation of their equation to $T = 299$ K gives $P_m = 6.5$ GPa, whereas we observed that CO at 299 K is a solid above about 2·6 GPa. This latter pressure is close to the 2·4 GPa melting pressure of N_2 at 299 K (Mills *et al.*, 1975).

We are unable to explain the striking difference between the CO melting curve inferred from the NMR measurements and that observed in the present X-ray work. Since it is now known that β-CO adjoins the melting curve from 95 to 299 K, we cannot ascribe a sudden change in slope $\mathrm{d}P_m/\mathrm{d}T$ to a crystal-structure change in this temperature range. Any mass-isotope effect in the heavier ^{13}CO sample used by Fukushima *et al.* (1977) would tend to lower the melting pressure. Also, their impurity content of about 1% Ar with a lesser amount of CH_4 was greater than ours, but hardly sufficient to explain the apparent large discrepancy in P_m. We note, finally, that the Fukushima *et al.* (1977) melting pressures tend to be larger than those reported by Clusius, Piesbergen & Varde (1960) at low pressures, up to 0·025 GPa.

It is possible to compare the CO molar volumes determined in the present X-ray study with those for N_2 extrapolated to the same P and T from equation-of-state (EOS) measurements (Mills *et al.*, 1975). The EOS study shows that nitrogen freezes at 299 K and 2·425 GPa into a solid with $V = 20{\cdot}42\ \text{cm}^3$. With the reasonable assumption that the compressibility of the solid is 0·9 times that of the liquid, we calculate from the EOS data that the molar volume of solid N_2 is $19{\cdot}96\ \text{cm}^3$ at 2·7 GPa and $18{\cdot}78\ \text{cm}^3$ at 3·6 GPa. The respective X-ray values for CO are 20·05 and $18{\cdot}69\ \text{cm}^3$, which differ by less than 0·5% from those for N_2.

We do not yet understand the chemical process that causes solid CO at 4·2 GPa to turn yellow brown when irradiated with a laser. We believe that near this pressure β-CO undergoes a phase transition to a new solid structure that is photosensitive. By analogy with the phase diagram for N_2, one might argue that the new sensitive phase is cubic *Pm*3*n* (Cromer *et al.*, 1981). Clearly more work is needed to characterize the chemical species that result from photoreaction of CO. We suspect that carbon dioxide and either carbon suboxide or elemental carbon may appear as products of photochemical disproportionation.

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