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Vapor Pressure of Carbon Monoxide in Condensed Phases*1

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A theoretical vapor pressure equation of the form $\log P + (3/2)\log T = a + b/T$ for a diatomic molecule was applied to carbon monoxide in condensed phases. The two parameters in the equation determined from experimental vapor pressure data were used to obtain values of the static lattice energy E_0, the zero point energy E_Z, the geometric mean frequency ω_g and the mean frequency of molecular rotation ω_R in the respective phases by the information of lattice vibrations at low temperatures. From the mean values of molecular rotation frequencies, the hights of the potential barrier for hindered rotations were estimated to be 360, 230±10 and 110 cal/mol respectively.

Molecular rotations in the condensed phases of carbon monoxide have been theoretically and experimentally investigated by several authors.1–5) However, there is little quantitative information about the state of hindered molecular rotation. Calorimetric studies showed that crystalline CO undergoes phase transition at 61.57°K and melts at 68.15°K.6,7) The low- and high-temperature phases are denoted by α and β, respectively.

We have measured vapor pressures7) of CO in two crystalline phases and liquid in the vicinity of the melting point. We will analyze these experimental vapor pressure data in terms of the quasi-harmonic theory of molecular vibrations, in which the normal modes of vibration are assumed to be harmonic, but have frequencies dependent upon the volumes of the solid and liquid. Values of the static lattice energy E_0 and the geometric mean frequency of the lattice vibrations ω_g in the respective phases of CO might be obtained from the analysis of vapor pressure. We will estimate the zero point energy E_Z and the mean frequency of molecular rotation ω_R or the height of the hindering potential V_0 by making use of the results of numerical calculation8) of lattice vibrations for solid carbon monoxide at low temperatures.

Vapor Pressure Equation for Carbon Monoxide

The theory of the vapor pressure of a diatomic crystal was derived by Salter9) along with monoatomic crystals, and applied to alkali halides by Leadbetter and Newsham.10) According to their results, the vapor pressure of a diatomic crystal at high temperatures can be related to the temperature by an equation of the form

$$\ln P + (3/2)\ln T = a + b/T \qquad (1)$$

The measurement for the vapor pressure of CO was made in the region 55° to 72°K as previously reported,7) and the results are listed in Table 1. An attempt has been made to find coefficients a and b which would make Eq. (1) fit these observed values in the α, β and liquid phases. The final equations are given in the following:

i) $55°\mathrm{K} < T <$ transition point

$$\log_{10}P + (3/2)\log_{10}T = -439.66/T + 11.27820, \qquad (2)$$

ii) transition point $< T <$ triple point

$$\log_{10}P + (3/2)\log_{10}T = -426.03/T + 11.06503, \qquad (3)$$

iii) $T >$ triplet point

$$\log_{10}P + (3/2)\log_{10}T = -384.90/T + 10.46265. \qquad (4)$$

At temperatures near melting point the contribution by the formation of lattice vacancies must be considered. Unfortunately no information on vacancy formation for CO crystal has been obtained

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1) G. E. Ewing, *J. Chem. Phys.*, **37**, 2250 (1962); G. E. Ewing and G. C. Pimentel, *ibid.*, **35**, 925 (1961).

2) B. C. Kohin, *ibid.*, **33**, 882 (1960).

3) L. Jansen, A. Michels and J. M. Lupton, *Physica*, **20**, 1235 (1954); *ibid.*, **20**, 1244 (1954).

4) M. W. Melhuish and R. L. Scott, *J. Phys. Chem.*, **68**, 2301 (1964).

5) R. F. Curl, Jr., H. P. Hopkins, Jr., and K. S. Pitzer, *J. Chem. Phys.*, **48**, 4064 (1968).

6) J. O. Clayton and W. F. Giauque, *J. Am. Chem. Soc.*, **54**, 2610 (1932).

7) T. Shinoda, T. Atake, H. Chihara, Y. Mashiko and S. Seki, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1619 (1966).

8) T. Shinoda and H. Enokido, *J. Phys. Soc. Japan*, **26**, 1353 (1969).

9) L. Salter, *Trans. Faraday Soc.*, **59**, 657 (1963).

10) A. J. Leadbetter and D. M. T. Newsham, *ibid.*, **61**, 1646 (1965).

TABLE 1. VAPOR PRESSURE OF SOLID AND LIQUID CO

T (°K)	P (Torr)	$P-P$ (Eqs. (2), (3) and (4)) (Torr)
Solid (α-form)		
54.779	4.54	+0.13
55.363	5.22	−0.05
55.926	6.21	−0.03
56.476	7.30	−0.04
57.017	8.54	−0.03
57.549	9.91	−0.05
58.068	11.36	−0.14
58.577	13.12	−0.09
59.125	15.21	−0.08
59.930	18.93	+0.07
60.488	21.92	+0.19
61.028	25.15	+0.28
Solid (β-form)		
61.871	31.08	+0.03
61.934	31.54	+0.04
62.319	34.40	−0.02
62.755	37.97	−0.03
63.571	45.60	+0.05
64.299	53.22	−0.11
65.020	61.99	−0.12
65.657	70.84	−0.02
66.287	80.60	+0.09
66.916	91.30	+0.08
67.462	101.61	+0.14
67.171	95.79	−0.10
67.708	106.38	−0.01
*67.999	112.71	+0.24
*67.985	112.52	+0.35
*68.074	114.32	+0.24
Liquid		
68.292	118.93	+0.08
68.296	118.83	−0.11
68.681	126.87	+0.04
69.590	147.18	0.00
70.490	169.82	−0.05
71.523	199.33	+0.03

* These data were omitted on analysis.

from analysis of the thermal properties at high temperatures, because the transition point for CO crystal is considerably close to its triple point. We have, therefore, omitted the vapor pressure data at temperatures right below the melting point. The deviation of the calculated values(horizontal line), using Eqs. (2), (3) and (4), from the observed ones is shown by open circles in Fig. 1.

Quasi-harmonic Analysis

The constants a and b of Eq. (1) give values of the static lattice energy E_0 and the geometric mean frequency for the translational and rotational lattice modes ω_g (ω_{gT} and ω_{gR}) on the basis of the theory for ideal gas, liquid and crystal, as follows:

$$\left.\begin{aligned} a &= 3\ln\omega_{gT} + 2\ln\omega_{gR} \\ &\quad + \tfrac{1}{2}\ln[(m/(2\pi))^3(1/\boldsymbol{k})] + \ln[(2\boldsymbol{I})/\boldsymbol{k}], \\ b &= E_0/(\boldsymbol{N}\boldsymbol{k}). \end{aligned}\right\} \qquad (5)$$

Here m is the molecular mass, $\boldsymbol{k}$ Boltzmann's constant, $\boldsymbol{I}$ its moment of inertia and $\boldsymbol{N}$ Avogadro's number. As the quantities E_0 and ω_g are temperature dependent, the values obtained by Eqs. (1) and (5) correspond to a certain mean temperature T_m in the respective phases. If we use the quasi-harmonic approximation, the effects of the change in volume of solid and liquid must be considered, but their variation over the respective temperature range of the analysis will be small. For the translational part of lattice vibrations we may expect the quasi-harmonic approximation to be adequate, because the most important parts in the translational motions of molecules are the spherical attractive dispersion and repulsive force between molecules.[8)]

We first calculated the static lattice energy $E_0(V_0)$ referring to the 0°K volume V_0 in terms of the same molecular interaction potential[8)] as used in the calculation of lattice vibrations for solid CO. The geometric mean frequency for the translational lattice modes $\omega_{gT}(0)$, and the translational and rotational zero point energies $E_{ZT}(V_0)$ and $E_{ZR}(V_0)$ referring to the 0°K volume have been estimated from frequency distributions in the harmonic approximation[8)] as is shown in Fig. 2.

On the other hand, the heat of sublimation of CO crystal at 0°K, $\Delta H_0(V_0)$, was calculated from experimental data on thermodynamic properties.[6,7)] The result is summarized in Table 2. The $E_0(V_0)$ can also be obtained from the relation

$$-E_0(V_T) = \Delta H_0(V_T) + E_{ZT}(V_T) + E_{ZR}(V_T), \qquad (6)$$

where V_T is the volume at T °K. The values of $E_0(V_0)$ calculated are −2337 cal/mol and −2423 cal/mol. The discrepancy between them is probably due to the uncertainty on the rotational potential energy of molecular interaction. We have therefore used the mean value of these values, −2380 cal/mol, as the value of $E_0(V_0)$, and then the difference, 43 cal/mol, has been subtracted from the value of the zero point energy due to rotation of molecules

TABLE 2. CALCULATION OF HEAT OF SUBLIMATION AT 0°K (in units of cal/mol)

$\int_0^{\mathrm{bp}} c_p(\mathrm{solid})\mathrm{d}T$	1003
Heat of vaporization (at bp)	1444
$\int_0^{\mathrm{bp}} C_p(\mathrm{gas})\mathrm{d}T$	−568
Correction for gas imperfection	17
Heat of sublimation at 0°K, $\Delta H_0(V)$	1896

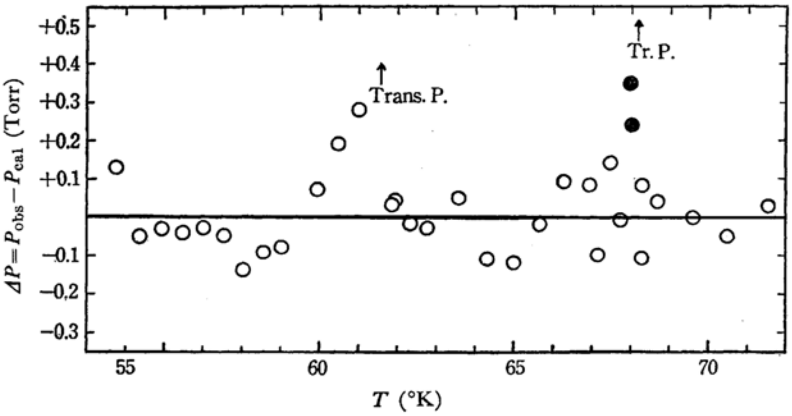

Fig. 1. Deviation of observed vapor pressure of CO from the calculated one by using Eqs. (2), (3) and (4). The black circles are data excluded on analysis.

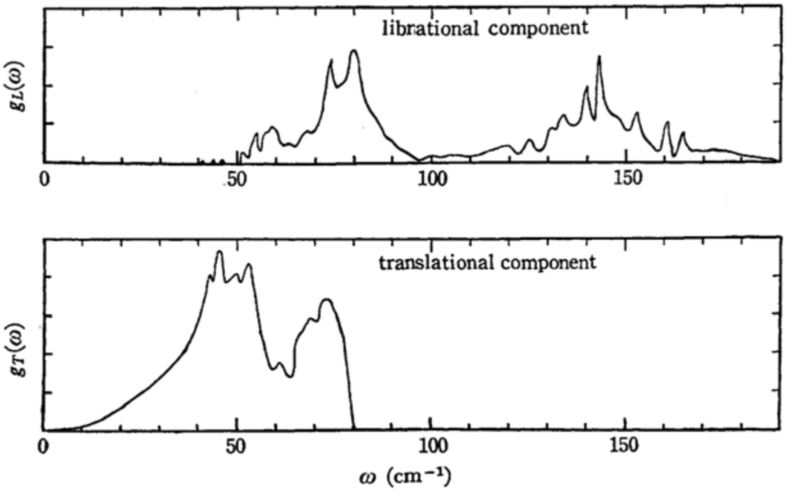

Fig. 2. The separated "translational" and "librational" distributions for CO crystal at 0°K, taken from Fig. 3 of Ref. 8.

$E_{ZR}(V_0)$ obtained by frequency distributions to make it consistent with other quantities.

To check the validity of the method adopted to estimate $E_0(V_0)$, $E_Z(V_0)$ and $\omega_g(0)$, the shape of the curve of the $\nu_D(n)$ function

$$\left.\begin{aligned}\nu_D(n) &= [(1/3)(n+3)\mu_n]^{1/n},\\ \mu_n &= (1/5N)\int_0^\infty \omega^n g(\omega)\mathrm{d}\omega,\end{aligned}\right\} \qquad (7)$$

where μ_n is the nth moment, has been established against n as is shown in Fig. 3 through use of the lattice frequency distributions in solid CO, since the $\nu_D(n)$ curve should be smooth, and $\nu_D(-3)$, $\nu_D(0)$ and $\nu_D(1)$ can be related to θ_0, ω_g and $E_Z(V_0)$ respectively, where θ_0 is the Debye characteristic temperature at 0°K and can be obtained from analyses of low temperature heat capacity data.[6,7]

The values of $E_0(V_0)$, $\omega_{gT}(V_0)$ and $E_Z(V_0)$ given above, have been used to analyze the vapor pressure for CO in the respective phases as fixed reference

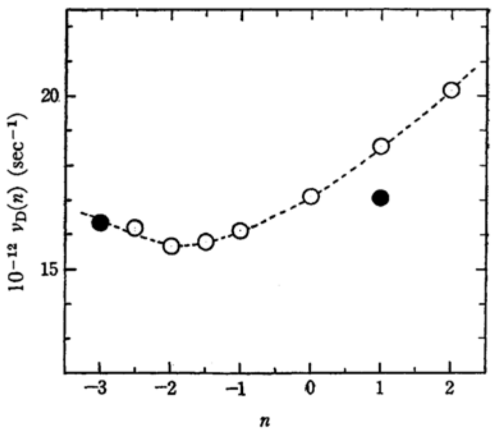

Fig. 3. The function $\nu_D(n) = [(1/3)(n+3)\mu_n]^{1/n}$ for CO. The open circles have been obtained from calculations and the black circles by analysis of the thermodynamic properties.

values.

The α-form; (54.8—61.0°K, $T_m=57.9$°K). The value of static lattice energy $E_0(V_{T_m})$ referring to the volume V_{T_m} at T_m in harmonic librational case has been estimated in the same way as for $E_0(V_0)$. In the quasi-harmonic approximation we may assume that the volume dependence of the static lattice energy is described by that of the zero point energy (*i.e.*, $\partial E_0/\partial V \simeq \partial E_Z/\partial V$). We may therefore estimate the zero point energy due to harmonic translation and libration of molecules corresponding to the mean temperature T_m, $E_Z(V_{T_m})(=E_{ZT}(V_{T_m})+E_{ZR}(V_{T_m}))$, by the approximate formula

$$E_0(V_{T_m})/E_0(V_0) \simeq E_Z(V_{T_m})/E_Z(V_0). \qquad (8)$$

We may also obtain $\Delta H_0(V_{T_m})$ as the difference between $|E_0(V_{T_m})|$ and $E_Z(V_{T_m})$ values from Eq. (6).

The deviation of the value of static lattice energy $E_0(V_{T_m})$ in harmonic libration from that derived directly by the constant a of Eq. (2), might be interpreted as CO molecules being in the state of not harmonic but anharmonic libration (or hindered rotation) at the mean temperature T_m. Thus, the difference between the two $E_0(V_{T_m})$ values has been treated as the decrease in the rotational zero point energy $E_{ZR}(V_{T_m})$. The general treatment for the anharmonic contribution to the lattice vibration has not been given. Barron[11] suggested that as a first approximation the anharmonic effects may be represented by a frequency shift in the quasi-harmonic expression. We have calculated $\omega_R(T_m)$, which can be replaced by the sum of the harmonic librational frequency plus the anharmonic frequency shift, using the resultant value of $E_{ZR}(V_{T_m})$ on the basis of the Einstein model of lattice vibration.

The geometric mean frequency for the rotational lattice modes $\omega_{gR}(T_m)$, has been obtained from the coefficient b in Eq. (2) using Eq. (5). We have assumed that the translational modes of lattice vibrations are harmonic but with frequencies dependent upon the volume, and the effect of the change in volume is expressed by that of the zero point energy due to translation of molecules. If we assume that

$$\omega(0)/\omega_g(0) \simeq \omega_R(T_m)/\omega_{gR}(T_m), \qquad (9)$$

where $\omega(T)=(1/5N)\int_0^\infty \omega g(\omega)\mathrm{d}\omega$, then the resultant value of $\omega_{gR}(T_m)$ can give the value of $\omega_R(T_m)$. This value, 29.3 cm^{-1}, is in excellent agreement with the value of $\omega_R(T_m)$ obtained from $E_{ZR}(V_{T_m})$, 29.4 cm^{-1}.

The β-form; (61.9—67.7°K, $T_m=65.0$°K). If the rotation of CO molecules in the β-phase is free, then the zero point energy due to rotation $E_{ZR}(V_{T_m})$ is zero and the translational lattice vibrations still possess the zero point energy $E_{ZT}(V_{T_m})$. The structure of CO crystal was studied by Vegard.[12] The molecular centers are located in face-centered cubic lattice sites in the α-phase, and in hexagonal close packed sites in the β-phase. The face-centered cubic and the hexagonal close-packed structures may be regarded as equivalent arrangement, as illustrated in Fig. 4. The β-phase crystal may therefore be taken as the face-centered cubic lattice which has the same density as the actual crystal at T_m. Since the major forces of interaction potential for the translational motion of molecules are the spherical dispersion and repulsive forces.[8] We may assume that the change in $E_{ZT}(V_{T_m})$ due to the α–β-phase transition is the only effect corresponding to the volume change. In the case of free rotation the static lattice energy $E_0(V_{T_m})$ can be calculated using $E_0(V_0)$ in free rotation at 0°K as the reference value, where $|E_0(V_0)|$ is equal to the sum of $\Delta H_0(V_0)$ plus $E_{ZT}(V_0)$. The difference between the value of static energy $E_0(V_{T_m})$ obtained from the slope a of vapor pressure Eq. (3) and that in the case of free rotation is equivalent to the zero point energy $E_{ZR}(V_{T_m})$ due to rotation of molecules in the β-phase. By the treatment described in analysis for the α-form, this value of $E_{ZR}(V_{T_m})$ gives the rotational frequency $\omega_R(T_m)$ of 22.0 cm^{-1}. Estimate of the value of $\omega_R(T_m)$ using the geometric mean frequency for the rotationals modes $\omega_{gR}(T_m)$ in the β-phase, which has been derived from the intercept b of Eq. (3), gives the resultant value of 23.7 cm^{-1}.

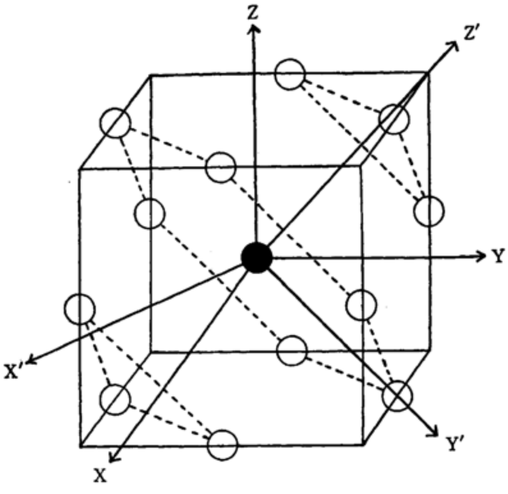

Fig. 4. The spatial arrangement of molecular centers in the face-centered cubic and the hexagonal close-packed lattices.

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[11] T. H. K. Barron, "Proceedings of the 1963 International Conference on Lattice Dynamics," ed. by R. F. Wallis, Pergamon Press, Inc., New York (1965), p. 247.

[12] L. Vegard, *Z. Physik.*, **61**, 185 (1930).

TABLE 3. RESULTS OF ANALYSIS OF THE VAPOR RRESSURE DATA FOR CO

	α-Form			β-Form		Liquid		
	Harmonic libration	Harmonic libration	α-CO	Free rotation	β-CO	Harmonic libration	Free rotation	Liquid CO
Mean temperature (T_m)	0°K	57.9°K	57.9°K	65.0°K	65.0°K	69.9°K	69.9°K	69.9°K
Density	1.04	0.95	0.95	0.929	0.929	0.846	0.846	0.846
Lattice constant	5.63 A	5.81 A	5.81 A	—	—	—	—	—
Spherical dispersion	−2903	−2403	—	—	—	−1971	—	—
Spherical repulsion	+1792	+1228	—	—	—	+845	—	—
Quadrupole interaction	−811	−693	—	—	—	−585	—	—
Anisotropic repulsion	−430	−277	—	—	—	−179	—	—
Anisotropic dispersion	+20	+17	—	—	—	+14	—	—
Dipole interaction	−5	0	—	—	—	0	—	—
Total (cal/mol)	−2337	−2128	—	—	—	−1876	—	—
$E_0(V_{T_m})$ (cal/mol)	−2380	−2167	−2012	−1886	−1951±2	−1911	−1719	−1761
$\Delta H_0(V_{T_m})$ (cal/mol)	1896	1726	1726	1688±2	1688±2	1541	1541	1541
$E_{ZT}(V_{T_m})$ (cal/mol)	222	202	202	198	198	178	178	178
$E_{ZR}(V_{T_m})$ (cal/mol)	262(305)	239	84	0	65±2	192	0	42
$\omega_R(T_m)$ (cm^{-1})	—	—	29.4 29.3	—	22.0 23.7	—	—	14.7 13.9
$\omega_g(T_m)$ (cm^{-1})	65.1	—	35.9	—	32.5	—	—	24.6

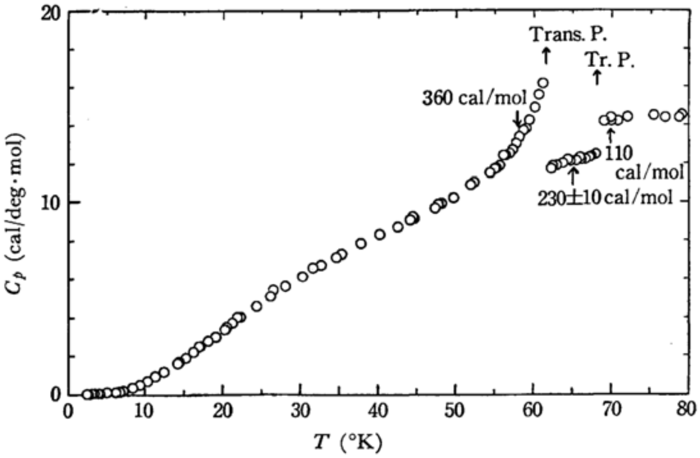

Fig. 5. The hindering potential barriers in the condensed phases, together with the experimental heat capacity curve of CO.

The Liquid in the Vicinity of the Melting Point; (T_m=69.9°K). We have adopted the cluster model for the liquid CO in the vicinity of its melting point. It may be assumed that the liquid consists of clusters containing 13 molecules,*2 and that the spatial arrangement of molecular centers in each cluster is the same as in a hypothetical solid, which has the density value at T_m determined by the extrapolation from the observed values. This is an approximation, which may be justified by the fact that only a continuous change in infrared spectral characteristic of CO occurs during the transition from liquid to solid.[1] In such liquids at least four different distances between the nearest neighboring molecules R_S, R_L, (R_L+R_{L-S}) and (R_L+2R_{L-S}) may be taken into consideration, where R_S is the nearest neighbor distance in a lattice having the density of a hypothetical solid, R_L in a lattice having the observed density of liquid CO at T_m, and R_{L-S} is the difference between R_S and R_L. We have assumed that all molecules in liquid are arranged with the statistical weights of these nearest neighbor distances of 6/13, 4/13, 2/13 and 1/13, respectively. The values of $E_0(V_{T_m})$, $E_{ZT}(V_{T_m})$ and $\Delta H_0(V_{T_m})$ in both harmonic libration and free rotation have been evaluated by the same treatment as was used in the solid phases. The value of $E_{ZT}(V_{T_m})$ evaluated as the difference between

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[*2] This is equal to the number of nearest neighbor molecules in addition to the one at center in face-centered cubic lattice.

$E_0(V_{T_m})$ obtained from the constant a in Eq. (4) and that in free rotation, leads to $\omega_R(T_m)=14.7\ \mathrm{cm}^{-1}$. This value is compared with the value of $13.9\ \mathrm{cm}^{-1}$ for $\omega_R(T_m)$ obtained from the constant b in Eq. (4).

Results and Analysis

Results of calculations are summarized in Table 3.

Discussion

Analysis of experimental vapor pressure data for CO has given us useful information about molecular motions in condensed phases. The values of $\omega_R(T_m)$ obtained in the respective phases may give the corresponding potential barriers, V_0, in which molecules are understood as the double-minimum two-dimensional rotators in a potential field of the type

$$V=(1/2)V_0(1-\cos 2\theta). \tag{10}$$

The Schrödinger equation for the rotational motion is

$$-(\hbar^2/2I)\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right)+(1/2)V_0(1-\cos 2\theta)\psi=E\psi. \tag{11}$$

Curl *et al.* have recently solved this problem and given a table of its energy levels.[13] If the above $\omega_R(T_m)$ corresponds to the separation of the two lowest levels, the values of the hindering potential, V_0, can be calculated by the help of Pitzer's table. The results are given in Fig. 5, together with the experimental heat capacity curve of CO.[6,7] There are no values available in literature to compare with the $\omega_R(T_m)$ or V_0 values derived here except for the V_0 in the region 10—30°K and in liquid, which were estimated to be 1.7 kcal/mol and 120 cal/mol by Curl *et al.*[13] and Ewing[1] from the low temperature heat capacity data and the band intensity of infrared spectra for liquid. The present values of V_0 are not unreasonable for the respective phases.

Although we have analyzed in terms of quasi-harmonic lattice theory, the static lattice energy, the geometric mean frequency, the zero point energy and the molecular rotational frequency (or hindering potential barrier) may serve to investigate molecular rotational state in the condensed phases for CO when the treatment of anharmonic effects is not clear. However, it must be noted that the derived values all correspond to some mean values over whole molecules in crystal and liquid CO at some mean temperature T_m over the temperature range of analysis. Much more exact treatment will be made by analysis of heat capacity data shown in Fig. 5 on the basis of the statistical theory taking into account cooperative phenomena in the condensed phases, in which adjacent molecules appear to rotate together like meshed gears.

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[13] R. F. Curl, Jr., H. P. Hopkins, Jr., and K. S. Pitzer, *J. Chem. Phys.*, **48**, 4064 (1968).