Phase Equilibrium Isotope Effects in Molecular Solids and Liquids.
Vapor Pressures of the Isotopic Carbon Dioxide Molecules*

Zayn Bilkadi⁺, Myung W. Lee and Jacob Bigeleisen

Department of Chemistry
University of Rochester
Rochester, New York 14627

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⁺ACS-PRF Fellow 1971-'3.

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Abstract

The vapor pressures of samples of CO_2 enriched in ^{13}C and ^{18}O have been compared with normal CO_2 over the temperature range $154^\circ - 217^\circ \text{ K}$. Over the entire temperature range the order of the vapor pressures is $P_{^{13}\text{CO}_2} > P_{^{12}\text{CO}_2} > P_{\text{C}^{18}\text{O}_2}$. The results are explained by the small shift in the internal vibrations, which dominate the carbon isotope effect, and hindered rotation in the solid and liquid. While the isotope effect on melting is small for carbon substitution, it is found to be large for oxygen substitution. Hindered rotation is the major contribution to the oxygen isotope effect in the solid, while the hindered translation is the most important contribution to the oxygen isotope effect in the liquid.

Model calculations of the logarithm of the reduced partition function ratios of the solid and liquid, $\ln(fc/fg)$, are made in an anharmonic version of the Stern-Van Hook-Wolfsberg cell model. These calculations give good agreement with the experimentally determined $\ln(fc/fg)$ values for the solid, liquid-vapor isotope fractionation measurements of Grootes, Mook and Vogel, and lattice dynamic calculations.

Introduction

Measurements of the vapor pressure ratio of isotopic substances have led to important information about the atomic and molecular motions in liquids and solids. The vapor pressure ratio is sensitive not only to the intermolecular interactions (translational as well as librational) in the condensed phases but also to the perturbation of the internal vibrational motions of the molecule by the intermolecular potential. A great deal of information concerning the translational motion in condensed phases has been obtained from the vapor pressure isotope effect studies of the rare gases.¹⁻⁵ Studies to date on molecular liquids and solids have provided unique information about hindered rotation,⁶⁻⁹ coupling of translation and rotation,¹⁰⁻¹⁵ coupling of vibration with rotation,^{8,16,17} perturbation of internal rotation¹⁸ and vibrations.¹⁷ The present study was undertaken to obtain information about molecular and intermolecular forces in solid and liquid CO₂ by the vapor pressure isotope effect method. Such studies complement information obtained from infra-red and raman spectroscopy¹⁹⁻²³ and inelastic neutron scattering.²⁴ Vapor pressure measurements were made of solid and liquid ¹²C¹⁶O₂, ¹³C¹⁶O₂ and ¹²C¹⁸O₂.

Experimental Method

The cryostat, pressure measurement techniques, and temperature measurement and control have been described previously.^{3,25} The carbon dioxide samples were isotopically impure. Corrections were made for the isotopic impurities by the method described below. The samples used were all derived from commercial sources. The isotope vapor pressure method at the sensitivity level used in this laboratory requires samples with chemical impurities below the 10 ppm level. The chemical purification of the commercial CO₂ samples was the simplest we have encountered in all of our vapor pressure isotope effect studies. The ¹²C¹⁶O₂ sample was derived from a Matheson 99.995% pure sample. The ¹²C¹⁸O₂ was purchased from Bio-Rad Laboratories; the ¹³C¹⁶O₂ was purchased from Prochem-BOC. The ¹³C in the ¹³CO₂ was obviously enriched by low temperature distillation of CO and the ¹³CO₂ sample supplied by Prochem was tenfold enriched in ¹⁸O and threefold enriched in ¹⁷O above natural abundance. To minimize the isotopic impurity corrections the sample of ¹³CO₂ was restored to natural abundance of the oxygen isotopes by equilibration with liquid water. Final chemical purification of each of the samples was accomplished by a sample bulb to bulb sublimation and passage through a helical trap immersed in a dry-ice bath. The latter removed traces of water. Air was removed by pumping on the solid at 77° K after successive freeze-thaw cycles. Final analyses of the samples

by low temperature gas chromatography and mass spectrometry established the maximum total impurities in each of the samples below the requisite 10 ppm level.

The isotopic composition of the samples used is given in Table I. For convenience in processing the experimental data each sample was reduced to an effective two component isotopic mixture by the use of the rule of the mean²⁶ and Raoult's law. The effective mole fractions of the samples used are given in Table II.²⁷

The vapor pressure of natural abundance CO₂ was used as the reference pressure, P_N. It was measured with a calibrated Bourdon gauge² and used as a thermometric standard in the range 154-197° K through the vapor pressure equation of Giaque and Egan²⁸

$$\log_{10} P(\text{int. cm Hg}) = \frac{-1354.210}{T} + 8.69903$$

(1)

$$+ 0.0015880 T - 4.5107 \times 10^{-6} T^2$$

In the temperature range 197-216° K the vapor pressure data of Meyers and Van Dusen²⁹ were used for normal CO₂. At the triple point of CO₂ the temperature scale of Meyers and Van Dusen is lower than the Giaque and Egan scale by 0.08° K. The vapor

pressure data of Meyers and Van Dusen for solid CO_2 were corrected to the Giauque and Egan temperature scale. Finally all of the data were corrected to the ice point $T = 273.15^\circ \text{ K}$. The working temperature scale which fits both the Giauque-Egan and Meyers-Van Dusen data for normal solid CO_2 between $155\text{--}216^\circ \text{ K}$ is

$$\begin{aligned} \log P \text{ (int. cm. Hg)} = & -11.313913 - 486.96889/T \\ & + 0.17433329 \times T - 0.6657019 \times 10^{-3} T^2 \\ & + 0.94685083 \times 10^{-6} T^3 \end{aligned} \quad (2)$$

Temperatures were measured independently to $\pm 0.02^\circ \text{ K}$ by a platinum resistance thermometer. The latter was calibrated by the use of 216.63° K as the triple point of natural CO_2 and the vapor pressure data of Giauque and Egan corrected to 273.15° K as the ice point.

The pressure differences (ΔP) between each of the samples " $^{12}\text{C}^{16}\text{O}_2$ ", " $^{13}\text{C}^{16}\text{O}_2$ " and " $^{12}\text{C}^{18}\text{O}_2$ " and a purified sample of normal CO_2 were measured by capacitance transducer manometers. The vapor pressures of the pure isotopes were calculated from the pressure measurements and the isotopic composition of the samples by the matrix equation

$$\begin{pmatrix} P_N \\ \Delta P \end{pmatrix} = \begin{pmatrix} Y_1^N & Y_2^N \\ (Y_1^N - Y_1^E) & (Y_2^N - Y_2^E) \end{pmatrix} \begin{pmatrix} P_1^O \\ P_2^O \end{pmatrix} \quad (3)$$

where P_N is the measured vapor pressure of the sample of normal CO_2 , P_1^O and P_2^O are the vapor pressures of two isotopically pure samples derived from measurements on samples with effective two component compositions Y_1^N , Y_2^N , Y_1^E , Y_2^E . The superscripts N and E refer to normal and enriched CO_2 respectively.

Results

The measured quantities, T , P_N , and ΔP along with the derived quantities $\ln(P'/P)$ and $\ln(fc/fg)$ are given in Tables III and IV. Table III gives the logarithm of the vapor pressure ratio, P'/P , for $^{12}\text{C}^{16}\text{O}_2/^{13}\text{C}^{16}\text{O}_2$ and the related reduced partition function ratio of the condensed phase referred to the ideal gas, $\ln(fc/fg)$ ($^{13}\text{CO}_2/^{12}\text{CO}_2$); the similar quantities for $^{12}\text{C}^{16}\text{O}_2/^{12}\text{C}^{18}\text{O}_2$ are given in Table IV. We note that over the temperature range of our measurements $P_{^{13}\text{CO}_2} > P_{^{12}\text{CO}_2} > P_{^{12}\text{C}^{18}\text{O}_2}$. The reduced partition function ratio is related to the vapor pressure ratio by the equation^{1,30}

$$\ln(fc/fg) = [1 + P(Bo - V_c/RT)] \ln(P'/P) \quad (4)$$

V_c is the molar volume of the condensed phase and Bo is the second virial coefficient when the equation of state is written

$$PV/RT = 1 + BoP + \dots$$

The temperature dependence of Bo is³¹

$$Bo \text{ (atm}^{-1}\text{)} = \frac{1.27672}{T} - \frac{743.592}{T^2} - \frac{204.348 \times 10^{-4}}{T^4} \quad (5)$$

The reduced partition function ratios were fitted to equations of the form

$$\ln(fc/fg) = A/T^2 - B/T - CT \quad (6)$$

The parameters A, B, and C are given in Tables V and VI for $^{13}\text{CO}/^{12}\text{CO}_2$ and $\text{C}^{18}\text{O}_2/\text{C}^{16}\text{O}_2$ respectively. Within the framework of the statistical mechanical theory of condensed phase isotope effects³⁰ extended to include anharmonic terms^{2,32} the quantities A, B and C have the following physical significance. A is related to the mean square force and torque in the condensed phase associated with the intermolecular potential; B is related to the zero point energy shifts of the internal vibrations from the gas to the condensed phase and includes anharmonic effects associated with the translational and librational motions in the condensed phase; C is a librational anharmonic effect. In Eq. (6) we neglect the small temperature independent term which arises from the coupling of internal and external modes.¹⁷

A plot of $T \ln(fc/fg)$ vs $10^3/T$ is given for both the $^{13}\text{CO}_2/^{12}\text{CO}_2$ and $\text{C}^{18}\text{O}_2/\text{C}^{16}\text{O}_2$ ratios. Also included are values derived from the isotope fractionation experiments in the liquid by Grootes, Mook and Vogel³³ for $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$. The latter yield results for the mixed molecule $\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$.

Discussion

The first complete calculation of the reduced partition function ratio of a pair of isotopic polyatomic molecules in a condensed phase, even in the harmonic oscillator approximations, was carried out by Stern, Van Hook and Wolfsberg¹⁷ within the framework of the general statistical mechanical theory of condensed phase isotope effects.³⁰ The important but simpler study of the liquid hydrogens carried out previously demonstrated the importance of quantum mechanical translation-rotation coupling.^{12,16,17,19} All of these studies used a simple model of the liquid with one molecule in a unit cell. The translational modes were assumed to have either a Debye or Einstein frequency spectrum. Through the choice of isotope independent external coordinates and an isotope independent F matrix, consistent with the neglect of Born-Oppenheimer corrections between the condensed and vapor phases, the S-VH-W method automatically includes mode coupling between all types of external and internal coordinates.¹⁶ In this paper we present the results of a calculation of $\ln(f_c/f_g)$ by the Stern-Van Hook-Wolfsberg method. We will compare the results of this model calculation with calculations made for a unit cell of the solid. The latter contains four molecules and the translational and librational modes are known. The four molecule per unit cell calculations by Lee³⁴ were made for the known structure^{19,35,36} and discrete translational and librational lattice modes. The external coordinates of

$^{12}\text{C}^{16}\text{O}_2$ were chosen as the basis coordinates for all the external modes, i.e., translation and rotation of all the isotopic CO_2 molecules. The method of calculation assumes that $\ln(fc/fg)$ can be calculated in the harmonic oscillator approximation for both the solid and gaseous phases, but that the $\mathbf{F}$ matrix elements associated with translation and rotation are temperature dependent. Within the harmonic oscillator approximation C in Eq. (6) is zero and A and B are given by³⁰

$$A = \frac{1}{24} (h/k)^2 \sum_{\text{ext}} (v_i'^2 - v_i^2) \quad (7)$$

$$B = (h/2k) \sum_{\text{int}} [(v_{ig}' - v_{il}') - (v_{ig} - v_{il})] + G(I, I') \quad (8)$$

The term $G(I, I')$ arises from non-classical rotation in the gas phase and is

$$G(I, I') = (hc/3k) (B_e - B_e') \quad (9)$$

where B_e is the rotational constant in wave numbers. The prime denotes the light isotope. The sums run over five external

coordinates and four internal coordinates. We shall also carry out a simple cell model calculation for the liquid.

Present spectroscopic information is inadequate to calculate the contributions of the internal vibrations to the B term in Eq. (6). A frequency shift of an internal vibration from the gas to the solid which gives a net difference between $[(\nu_i' - \nu_i)_g - (\nu_i' - \nu_i)_s]$ of 0.06 cm^{-1} contributes 2×10^{-4} to $\ln(f_c/f_g)$ at 180° K . This is the magnitude of the logarithm of the $(^{13}\text{CO}_2/^{12}\text{CO}_2)$ ratio. The $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio has no rotational effect, except from coupling terms. It is obvious that the shift in the internal vibrations dominates the magnitude and determines the sign of the logarithm of the $^{13}\text{CO}_2/^{12}\text{CO}_2$ ratio. After a preliminary estimate of the translational effect in $^{13}\text{CO}_2/^{12}\text{CO}_2$, the experimentally determined $\ln(f_c/f_g)$ for $^{13}\text{CO}_2/^{12}\text{CO}_2$ was used to determine the total shift in the asymmetric stretching and bending force constants. There is no carbon isotope shift in the symmetric stretching frequency. The shift in the latter force constant was determined to conform with observed spectroscopic data and to fit the B term in Eq. (6) for $\text{C}^{18}\text{O}_2/\text{C}^{16}\text{O}_2$. If one applies an anharmonic correction to Eq's (7,8), then B in Eq. (6) is

$$B = B(8) + A_{\text{tr}}^{\circ} \alpha_{\text{tr}} + A_{\text{rot}}^{\circ} \alpha_{\text{rot}} \quad (10)$$

where $B(8)$ is given by Eq. (8) and α_{tr} and α_{rot} are defined eq'ns (11) and (12) respectively.

$$A_{tr} = A_{tr}^{\circ} (1 - \alpha_{tr} T) \quad (11)$$

$$A_{rot} = A_{rot}^{\circ} (1 - \alpha_{rot} T - \beta_{rot} T^3) \quad (12)$$

The anharmonic constant for translation, α_{tr} , was determined from the principle of corresponding states for $\langle v^2_U \rangle_{tr}$, which has been established experimentally for the rare gases.^{1,2,3} Thus, the results of Lee, Fuks and Bigeleisen for solid argon,

$$\langle v^2_U \rangle_{Ar} = \langle v^2_U \rangle_{Ar}^{\circ} (1 - 1.956 \times 10^{-3} T),$$

lead to a value of 7.57×10^{-4} for $\alpha_{tr}(\text{CO}_2)$. In arriving at $\alpha_{tr}(\text{CO}_2)$ we define $T^* = T/T(\text{triple point})$. This definition avoids the small correction factor, β , which Lee, Eshelman and Bigeleisen³ found necessary when T^* is defined as kT/ϵ . ϵ is the depth of the intermolecular potential.

The anharmonic rotational constants α_{rot} and β_{rot} were determined from the temperature dependence of the Raman spectral data of solid CO_2 measured by Cahill and Leroi.³⁶ A least square fit was made to their data to give α_{rot} and β_{rot} through the relation

$$\sum v^2(\text{rot}) = K (1 - \alpha_{\text{rot}} T - \beta_{\text{rot}} T^3)$$

Thus we find for solid CO_2

$$A_{\text{rot}} = A_{\text{rot}}^{\circ} (1 - 5.5 \times 10^{-4} T - 1.95 \times 10^{-8} T^3)$$

where A° is $A(7)$, the harmonic value for the librational modes.

The following relationships

$$8v_{\text{rot}}^2(1) = \sum_{\text{lib}}^8 v_{\text{lib}}^2 \quad (13)$$

$$12v_{\text{tr}}^2(1) = \sum_{\text{tr}}^9 v_{\text{tr}}^2 \quad (14)$$

suffice to complete the 1 molecule per unit cell model. In Eq'ns (13) and (14), v_{lib}^2 and v_{tr}^2 are the spectroscopically¹⁹⁻²⁴ determined librational and translations frequencies respectively. The notation $v_{\text{rot}}^2(1)$ and $v_{\text{tr}}^2(1)$ defines two sets of Einstein frequencies for the rotation and translation respectively in the 1 molecule per unit cell model. The Einstein frequencies for $^{12}\text{CO}_2$ are 80.6 cm^{-1} and 105.7 cm^{-1} for $v_{\text{tr}}(1)$ and $v_{\text{rot}}(1)$ respectively. The $\underline{F}$ matrices for the gas and solid are given in Table VII. Within the one molecule per unit cell model a

translation-libration $\underline{F}$ matrix element, $f_{68} = f_{79}$, is necessary to fit the four molecule per unit cell calculation of $^{12}\text{C}^{16}\text{O}^{18}\text{O}$. Such interaction terms in the $\underline{F}$ matrix were found necessary to reproduce the experimental $\ln(f_c/f_g)$ data on the deuterioethylenes.³² The $\underline{G}$ matrix elements were derived according to the formulation given by Stern, Van Hook and Wolfsberg and are tabulated elsewhere.²⁷ The shifts in the internal frequencies calculated from the $\underline{F}$ matrix in Table VII are compared with spectroscopic observations in Table VIII. The contributions of the various modes; translation, rotation, internal vibration, and non-classical rotation to the various terms A/T^2 , B/T , and CT in Eq. (6) are tabulated in Tables V and VI for $\ln(f_c/f_g)$ ($^{13}\text{CO}_2/^{12}\text{CO}_2$) and ($\text{C}^{18}\text{O}_2/\text{C}^{16}\text{O}_2$) respectively. We note that the A term, translation and rotation in the solid, has been calculated entirely from spectroscopic data in quantitative agreement with the least square constants. The total B term is also in excellent agreement with the experimental values, but it has been adjusted to fit the experimental B terms. The significant comparison on the B terms is really in Table VIII where we see that the frequency shifts from gas to solid calculated from the isotope vapor pressure data are consistent with the spectroscopic observations. Since they are calculated from the $\underline{FG}$ matrices they are self consistent and do not show the scatter of the experimental observations. It is rather remarkable that even the CT term

from the isotopic vapor pressure measurements is of the same order of magnitude as that calculated from the Raman data. The total A/T^2 term in $\ln(fc/fg)$ calculated by the simple 1 molecule per unit cell model with Einstein frequencies agrees rather well with the detailed calculation from the 4 molecule per unit cell. This is a consequence of the small interaction between the internal and external modes in CO_2 and the fact that the first quantum correction is an excellent approximation of the total contribution of the external modes to $\ln(fc/fg)$. This dictated our definition of $v_{\text{tr}}(1)$ and $v_{\text{rot}}(1)$.

For ^{18}O substitution for ^{16}O in CO_2 the A/T^2 term dominates the condensed phase isotope effect in the solid. We shall give a simple calculation of $\ln(fc/fg)$ for $(\text{C}^{16}\text{O}^{18}\text{O})/\text{C}^{16}\text{O}_2$ in the approximation

$$\ln fc/fg \cong A/T^2 \quad (15)$$

where A is calculated by the mean square torque method.^{11,12,37}

$$A = [H^2/(24k^3T)] \left\{ \left(\frac{1}{M'} - \frac{1}{M} \right) \langle (\nabla U)^2 \rangle + \left(\frac{1}{I'} - \frac{1}{I} \right) \langle (OU)^2 \rangle \right. \\ \left. + (Z - Z')^2 \langle (\nabla U \times \hat{Z})^2 \rangle / I' \right\} \quad (16)$$

$\langle (OU)^2 \rangle$ is the mean square torque on the molecule. For an asymmetrical linear molecule, e.g., $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, it is related to the mean square torque, $\langle (O'U)^2 \rangle$, in the symmetrical isotopic molecule $^{12}\text{C}^{18}\text{O}_2$ by the relation

$$\langle (OU)^2 \rangle = \langle (O'U)^2 \rangle + (z - z')^2 \langle (\nabla U \times \hat{z})^2 \rangle \quad (17)$$

where z' and z are the centers of gravity of the symmetric and asymmetric molecules respectively and $\hat{z}$ is a unit vector along the molecular axis. The harmonic diagonal F matrix elements in Table VII lead to the following values for the three terms in Eq. (16) for $\ln(fc/fg)$ ($\text{C}^{18}\text{O}^{18}\text{O}/\text{C}^{18}\text{O}_2$): $75.93(^{\circ}\text{K})^2$ translation, $110.05(^{\circ}\text{K})^2$ rotation, and $3.64(^{\circ}\text{K})^2$ translation-rotation coupling. The value of $\ln(fc/fg)$ ($\text{C}^{18}\text{O}^{18}\text{O}/\text{C}^{18}\text{O}_2$) in this A/T^2 approximation is compared with the complete calculation in Fig. 1. The results of the latter are given in Table IX.

Our experimental data for $\ln(fc/fg)$ ($\text{C}^{18}\text{O}_2/\text{C}^{16}\text{O}_2$) extend past the triple points of both substances and 0.3°K into the liquid range. They suffice to determine the isotope effect on melting. From these data we can derive the necessary parameters to calculate $\ln(fc/fg)$ and the logarithm of the liquid-vapor fractionation factor in the neighborhood of the triple point for comparison with the experimental data of Grootes, Mook and Vogel.³³ We shall use the simple cell model of the liquid and assume that the internal F matrix elements are the same in the liquid as

in the solid. We shall neglect anharmonic effects in the liquid and derive the harmonic values of A/T^2 associated with translation and rotation from the solid values. We shall assume the same translation-rotation coupling in the liquid as in the solid. Previous work on the rare gases shows that

$$(A_l/A_s)_{\text{trans}} \approx (V_s/V_l) \quad (18)$$

where A_l and A_s refer to the A values in Eq. (7) and V_l and V_s are the molar volumes of liquid and solid respectively. With these assumptions the partition function ratio in the liquid phase can be written

$$\ln(fc/fg)_{\text{liq}} = (V_s/V_l) \frac{A_{\text{tr}(s)}}{T^2} + \frac{A_{\text{rot}(l)}}{T^2} - \frac{B(s)}{T} \quad (19)$$

where $B(s)$ is calculated from the matrix elements in Table VII and Eq. (8). The molal volumes of solid and liquid near the triple point are 29.09 and 37.37 cc mole⁻¹ respectively.^{38,39} The experimental value of $\ln(fc/fg)_{\text{liq}}$ ($C^{18}O_2/C^{16}O_2$) at the triple point now suffices to determine the pseudo harmonic rotational force constant in the liquid from Eq'ns (18), (19) and the known value of $A_{\text{tr}(s)}$. The term $A_{\text{rot}(l)}$ is related to the force constant by

$$A_{\text{rot(l)}} = \frac{2}{24} \left(\frac{\pi}{k} \right)^2 \left(\frac{1}{I'} - \frac{1}{I} \right) \left(\frac{\partial^2 U_{\text{rot}}}{\partial \theta^2} \right)_1 \quad (20)$$

The contributions of translation, rotation and internal vibration to $\ln(fc/fg)_1$ for $(C^{16}O^{18}/C^{16}O_2)_1$ and $(^{13}CO_2/^{12}CO_2)_1$, have been calculated through Eq'ns (8), (19) and (20) and are given in Table X. They are compared with the independent isotope fractionation data in Fig. 1. The agreement between theory and experiment is excellent. In the case of oxygen substitution, $(C^{18}O_2/C^{16}O_2)_1$, hindered rotation is about 60% of the isotope effect in the solid, but only 30% of the effect in the liquid. The ratio of the translational contribution to the oxygen condensed phase isotope effects in the solid to that in the liquid is 1.22; the similar ratio for rotation is 4.2. The onset of almost free rotation in the liquid explains the much larger isotope effect on melting in a polyatomic molecule when isotopic substitution changes the moment of inertia than the typical 20% effects observed for the rare gases.

Table I

Isotopic Composition of the Carbon Dioxide Samples (in percent)

Species	<u>"$^{12}\text{C}^{16}\text{O}_2$"</u>	<u>Sample "$^{12}\text{C}^{18}\text{O}_2$"</u>	<u>"$^{13}\text{C}^{16}\text{O}_2$"</u>
$^{12}\text{C}^{16}\text{O}^{16}\text{O}$	98.4	0.4	11.4
$^{12}\text{C}^{17}\text{O}^{16}\text{O}$	0.1	0.2	-
$^{12}\text{C}^{16}\text{O}^{18}\text{O}$	0.4	11.4	-
$^{12}\text{C}^{17}\text{O}^{18}\text{O}$	-	2.4	-
$^{12}\text{C}^{18}\text{O}^{16}\text{O}$	-	84.5	-
$^{13}\text{C}^{16}\text{O}^{16}\text{O}$	1.1	-	88.1
$^{13}\text{C}^{16}\text{O}^{17}\text{O}$	-	-	0.1
$^{13}\text{C}^{18}\text{O}^{16}\text{O}$	-	1.0	-
$^{13}\text{C}^{16}\text{O}^{18}\text{O}$	-	0.1	0.4

Table II.

Effective Mole Fractions of Ordinary and Enriched Samples (in percent)

<u>Sample</u>	<u>$^{12}\text{C}^{16}\text{O}^{16}\text{O}$</u>	<u>$^{13}\text{C}^{16}\text{O}^{16}\text{O}$</u>	<u>$^{12}\text{C}^{18}\text{O}^{16}\text{O}$</u>
" $^{13}\text{C}^{16}\text{O}_2$ "	11.85	88.15	
" $^{12}\text{C}^{16}\text{O}_2$ "	98.9	1.1	
" $^{12}\text{C}^{18}\text{O}_2$ "	6.90		93.10
" $^{12}\text{C}^{16}\text{O}_2$ "	99.77		0.23

Table III. Observed vapor pressures and reduced partition function ratios for $^{13}\text{CO}_2/^{12}\text{CO}_2$.

Run No.	T (°K)	P_N^a	A^a	B^a	C^a
16	154.14	11.18	-0.24	-0.28	-0.28
47	155.67	13.72	-0.33	-0.37	-0.37
48	156.41	15.11	-0.28	-0.33	-0.32
18	156.84	15.90	-0.37	-0.42	-0.42
19	158.10	18.67	-0.24	-0.27	-0.27
49	158.57	19.79	-0.25	-0.29	-0.29
20	158.95	20.70	-0.24	-0.28	-0.28
21	159.52	22.20	-0.31	-0.36	-0.36
22	160.70	25.64	-0.33	-0.38	-0.38
50	160.79	25.94	-0.23	-0.27	-0.27
23	161.94	29.71	-0.29	-0.33	-0.33
24	162.01	29.98	-0.36	-0.41	-0.41
52	165.55	46.09	-0.20	-0.23	-0.23
25	166.10	48.19	-0.22	-0.25	-0.25
53	167.68	57.12	-0.19	-0.21	-0.21
27	168.04	59.82	-0.16	-0.18	-0.18
28	168.90	65.96	-0.17	-0.19	-0.19
54	170.16	75.72	-0.18	-0.21	-0.21
55	171.86	90.68	-0.17	-0.19	-0.19
29	172.19	93.81	-0.18	-0.21	-0.21
56	173.64	109.11	-0.18	-0.21	-0.21
57	175.39	130.83	-0.19	-0.22	-0.21
58	177.25	157.49	-0.20	-0.23	-0.23
59	179.25	191.72	-0.18	-0.20	-0.20

Table III.(continued)

31	179.78	201.73	-0.20	-0.23	-0.23
60	181.00	226.82	-0.19	-0.22	-0.22
61	183.07	275.69	-0.19	-0.21	-0.21
32	184.42	312.26	-0.24	-0.27	-0.27
62	185.28	337.63	-0.20	-0.22	-0.22
63	187.30	404.78	-0.20	-0.23	-0.23
33	187.74	419.71	-0.16	-0.18	-0.18
64	189.93	509.31	-0.20	-0.23	-0.22
34	192.84	651.88	-0.21	-0.24	-0.23
65	192.99	657.15	-0.21	-0.24	-0.23
66	194.59	753.03	-0.21	-0.24	-0.24
36	196.81	900.98	-0.23	-0.27	-0.26
37	197.52	954.20	-0.25	-0.29	-0.28

Table III. (continued)

67	199.34	1102.54	-0.27	-0.30	-0.30
69	201.79	1333.22	-0.26	-0.30	-0.29
70	202.87	1447.65	-0.28	-0.32	-0.31
71	203.85	1559.22	-0.30	-0.35	-0.33
72	205.29	1736.43	-0.33	-0.37	-0.36
93	207.08	1980.96	-0.26	-0.29	-0.28
94	207.27	2008.70	-0.29	-0.33	-0.31
95	207.66	2066.27	-0.29	-0.33	-0.31
97	208.03	2123.03	-0.24	-0.27	-0.26
73	208.49	2194.97	-0.28	-0.32	-0.30
74	209.35	2334.71	-0.27	-0.31	-0.30
98	210.78	2587.46	-0.24	-0.27	-0.26
99	210.98	2623.43	-0.17	-0.19	-0.18
100	211.16	2656.68	-0.14	-0.16	-0.15
101	211.28	2680.20	-0.25	-0.28	-0.27
102	211.34	2691.71	-0.19	-0.22	-0.21
104	213.24	3074.76	-0.25	-0.28	-0.26
75	213.32	3092.08	-0.29	-0.33	-0.31
105	213.33	3095.97	-0.27	-0.31	-0.29
106	213.36	3102.77	-0.24	-0.28	-0.26
107	213.39	3107.75	-0.23	-0.27	-0.25
108	213.39	3107.75	-0.35	-0.40	-0.37
110	213.39	3108.82	-0.25	-0.29	-0.27
109	213.40	3110.95	-0.33	-0.38	-0.35

Table III (continued)

113	213.44	3118.43	-0.27	-0.31	-0.29
111	213.46	3124.00	-0.34	-0.39	-0.36
114	213.48	3128.55	-0.26	-0.30	-0.28
115	213.52	3137.22	-0.27	-0.31	-0.29
116	213.56	3145.36	-0.25	-0.29	-0.27
117	213.59	3151.81	-0.26	-0.30	-0.28
118	213.73	3182.25	-0.27	-0.31	-0.29
119	213.75	3187.73	-0.26	-0.30	-0.28
120	213.78	3193.19	-0.25	-0.28	-0.26
121	213.85	3208.52	-0.28	-0.32	-0.29
122	213.90	3219.56	-0.26	-0.30	-0.28
123	213.97	3236.13	-0.22	-0.25	-0.24
124	214.22	3291.41	-0.24	-0.27	-0.26
125	214.28	3306.84	-0.24	-0.27	-0.25
127	214.39	3332.47	-0.25	-0.29	-0.27
126	214.42	3338.05	-0.22	-0.26	-0.24
130	214.44	3342.91	-0.27	-0.31	-0.29
128	214.44	3344.07	-0.28	-0.32	-0.29
129	214.45	3345.21	-0.32	-0.37	-0.34
131	214.51	3359.77	-0.31	-0.35	-0.33
133	214.57	3373.85	-0.39	-0.45	-0.42
132	214.61	3381.81	-0.25	-0.29	-0.27
134	214.67	3396.95	-0.28	-0.32	-0.30
136	214.79	3424.82	-0.28	-0.33	-0.30

Table III.(continued)

135	214.90	3450.56	-0.22	-0.25	-0.23
137	214.96	3466.15	-0.21	-0.24	-0.22
138	215.06	3489.42	-0.30	-0.35	-0.32
139	215.36	3561.23	-0.33	-0.37	-0.35
140	215.65	3633.06	-0.31	-0.36	-0.33
141	216.24	3783.10	-0.25	-0.29	-0.27
144	216.38	3819.04	-0.25	-0.29	-0.27
145	216.43	3832.45	-0.26	-0.30	-0.28
146	216.50	3851.90	-0.26	-0.30	-0.28
148	216.53	3858.66	-0.27	-0.30	-0.28
147	216.54	3860.66	-0.24	-0.28	-0.26
149	216.58	3871.44	-0.37	-0.42	-0.39
150	216.63	3885.10	-0.47	-0.54	-0.50

^a Pressure in int.cm. Hg.; $A=10^3 \Delta P/P_N$; $B=10^3 \ln P'/P$;
 $C=10^3 \ln (f_c/f_g)$.

Table IV. Observed vapor pressure and reduced partition function ratios for $C^{18}O_2/C^{16}O_2$.

Run No.	T° (K)	P_N^a	A^a	B^a	C^a
16	154.14	11.18	11.30	12.23	12.23
47	155.67	13.72	11.40	12.35	12.34
48	156.41	15.11	11.18	12.10	12.09
18	156.84	15.90	10.64	11.52	11.51
19	158.10	18.67	11.15	12.08	12.07
49	158.57	19.79	10.99	11.90	11.89
20	158.95	20.70	11.02	11.94	11.92
21	159.52	22.20	10.86	11.76	11.74
22	160.70	25.64	10.64	11.52	11.51
50	160.79	25.94	10.81	11.70	11.69
23	161.94	29.71	10.61	11.48	11.47
24	162.01	29.98	10.47	11.33	11.32
52	165.55	46.09	10.03	10.85	10.83
25	166.10	48.19	10.12	10.96	10.93
53	167.68	57.12	9.94	10.75	10.73
27	168.04	59.82	9.88	10.70	10.67
28	168.90	65.96	9.72	10.52	10.49
54	170.16	75.72	9.61	10.40	10.37
55	171.86	90.68	9.40	10.17	10.14
29	172.19	93.81	9.40	10.16	10.13
56	173.64	109.11	9.19	9.94	9.90
57	175.39	130.83	8.99	9.72	9.67
58	177.25	157.49	8.77	9.49	9.44
59	179.25	191.72	8.57	9.27	9.21

Table IV. (continued)

31	179.78	201.73	8.52	9.21	9.15
60	181.00	226.82	8.36	9.04	8.97
61	183.07	275.69	8.15	8.81	8.74
32	184.42	312.26	8.04	8.69	8.60
62	185.28	337.63	7.94	8.58	8.49
63	187.30	404.78	7.74	8.37	8.27
33	187.74	419.71	7.85	8.48	8.38
64	189.93	509.31	7.58	8.19	8.07
34	192.84	651.88	7.24	7.82	7.68
65	192.99	657.15	7.33	7.92	7.78
66	194.59	753.03	7.21	7.78	7.63
36	196.81	900.98	7.01	7.58	7.40
37	197.52	954.20	6.97	7.53	7.34

Table IV. (continued)

67	199.34	1102.54	6.83	7.38	7.17
69	201.79	1333.22	6.64	7.18	6.94
70	202.87	1447.65	6.54	7.07	6.82
71	203.85	1559.22	6.46	6.98	6.72
72	205.29	1736.43	6.43	6.95	6.67
93	207.08	1980.96	6.34	6.85	6.55
94	207.27	2008.70	6.30	6.80	6.50
95	207.66	2066.27	6.28	6.78	6.47
97	208.03	2123.03	6.29	6.79	6.47
73	208.49	2194.97	6.19	6.68	6.36
74	209.35	2334.71	6.17	6.66	6.32
98	210.78	2587.46	6.11	6.60	6.23
99	210.98	2623.43	6.09	6.57	6.21
100	211.16	2656.68	6.13	6.62	6.24
101	211.28	2680.20	6.09	6.58	6.20
102	211.34	2691.71	6.07	6.56	6.18
104	213.24	3074.76	6.01	6.49	6.08
75	213.32	3092.08	6.29	6.79	6.36
105	213.33	3095.97	6.01	6.49	6.07
106	213.36	3102.37	6.00	6.48	6.06
107	213.39	3107.75	6.04	6.53	6.11
108	213.39	3107.75	6.02	6.50	6.08
110	213.39	3108.82	6.01	6.49	6.07
109	213.40	3110.95	6.03	6.51	6.09

Table IV. (continued)

113	213.44	3118.43	5.98	6.46	6.04
111	213.46	3124.00	6.00	6.47	6.05
114	213.48	3128.55	5.98	6.46	6.04
115	213.52	3137.22	5.98	6.46	6.04
116	213.56	3145.36	5.99	6.46	6.04
117	213.59	3151.81	5.99	6.46	6.04
118	213.73	3182.25	5.98	6.46	6.03
119	213.75	3187.73	5.96	6.44	6.01
120	213.78	3193.19	5.99	6.47	6.04
121	213.85	3208.52	5.93	6.41	5.98
122	213.90	3219.56	5.95	6.42	6.00
123	213.97	3236.13	5.98	6.45	6.02
124	214.22	3291.41	5.87	6.33	5.90
125	214.28	3306.84	5.93	6.40	5.97
127	214.39	3332.47	5.73	6.18	5.76
126	214.42	3338.05	6.06	6.54	6.09
130	214.44	3342.91	5.80	6.27	5.84
128	214.44	3344.07	5.74	6.20	5.77
129	214.45	3345.21	5.70	6.15	5.73
131	214.51	3359.77	5.84	6.30	5.87
133	214.57	3373.85	5.72	6.17	5.75
132	214.61	3381.81	5.87	6.34	5.90
134	214.67	3396.95	5.89	6.36	5.92
136	214.79	3424.82	5.95	6.42	5.97

Table IV. (continued)

135	214.90	3450.56	5.88	6.35	5.91
137	214.96	3466.15	6.13	6.62	6.15
138	215.06	3489.42	5.96	6.43	5.98
139	215.36	3561.23	6.14	6.63	6.15
140	215.65	3633.06	5.91	6.39	5.92
141	216.24	3783.10	5.91	6.38	5.90
144	216.38	3819.04	5.89	6.36	5.87
145	216.43	3832.45	5.90	6.37	5.89
146	216.50	3851.90	5.88	6.35	5.86
148	216.53	3858.66	5.78	6.24	5.76
147	216.54	3860.66	6.28	6.78	6.26
149	216.58	3871.44	5.84	6.31	5.82
150	216.63	3885.10	6.11	6.60	6.09

Table IV. (continued)

294	216.63	3890.42	5.66	6.11	5.64
295	216.64	3891.32	5.58	6.02	5.56
296	216.64	3892.43	5.48	5.92	5.46
297	216.64	3892.43	5.39	5.82	5.37
298	216.64	3892.68	5.29	5.71	5.27
299	216.65	3893.86	5.12	5.52	5.10
300	216.66	3894.46	4.98	5.38	4.96
301	216.66	3894.99	4.83	5.21	4.81
302	216.67	3897.18	4.67	5.04	4.65
303	216.68	3898.28	4.46	4.81	4.44
304	216.68	3899.27	4.28	4.61	4.25
305	216.69	3900.54	4.00	4.31	3.98
306	216.70	3901.79	3.78	4.08	3.76
307	216.71	3903.65	3.60	3.89	3.58
308	216.72	3904.63	3.44	3.71	3.42
309	216.73	3906.37	3.27	3.53	3.25
310	216.73	3906.37	3.22	3.48	3.20
311	216.73	3906.74	3.18	3.43	3.16
312	216.73	3907.49	3.15	3.40	3.13
313	216.73	3907.64	3.14	3.38	3.12
314	216.72	3905.98	3.14	3.38	3.12
315	216.74	3909.57	3.14	3.38	3.12
316	216.75	3910.17	3.14	3.39	3.12
317	216.75	3910.59	3.15	3.39	3.13

Table IV. (continued)

318	216.76	3911.58	3.15	3.40	3.13
320	216.77	3913.43	3.16	3.41	3.14
321	216.78	3916.14	3.17	3.42	3.15
322	216.79	3917.78	3.18	3.43	3.16
323	216.80	3919.40	3.18	3.43	3.16
324	216.81	3920.75	3.19	3.43	3.17
325	216.83	3924.42	3.19	3.44	3.17
326	216.86	3928.65	3.48	3.75	3.45
327	216.96	3946.34	3.27	3.52	3.25

^aPressure in int. cm. Hg; $A=10^3 \Delta P/P_N$, $B=10^3 \ln P'/P$,
 $C=10^3 \ln(fc/fg)$.

Table V

Contribution to the Solid-Vapor
Reduced Partition Function Ratios
in the Isotopic CO₂ Molecules (¹³CO₂/¹²CO₂)

		T^{-2}	T^{-1}	T
Translation	(4)	38.872	-0.029	
Translation	(1)	35.819	-0.027	
Libration	(4)			
Libration	(1)	3.054	-0.002	-5.97×10^{-8}
Internals	(4)		-0.231	
Internals	(1)		-0.216	
G(I, I')				
Total	(4)	38.872	-0.260	0
Total	(1)	38.873	-0.245	-5.97×10^{-8}
Experimental (least square)		38.9	-0.261	

(4) = 4 molecules/unit cell

(1) = 1 molecule/unit cell

Table VI

Contributions to the Solid-Vapor
Reduced Partition Function Ratios
in the Isotopic CO₂ Molecules (C¹⁸O₂/C¹⁶O₂)

		T^{-2}	T^{-1}	T
Translation	(4)	145.54	-0.110	
Translation	(1)	142.89	-0.108	
Libration	(4)	207.88	-0.114	-4.06×10^{-6}
Libration	(1)	210.53	-0.116	-4.11×10^{-6}
Internals	(4)		-0.091	
Internals	(1)		-0.073	
G(I, I')			+0.021	
Total	(4)	353.42	-0.295	-4.06×10^{-6}
Total	(1)	353.42	-0.277	-4.11×10^{-6}
Experimental (least square)		353.4	-0.304	-1.228×10^{-6}

(4) = 4 molecules/unit cell

(1) = 1 molecule/unit cell

Table VII

CO₂ F-Matrix (in millidynes Å⁻¹)* (1 molecule per cell)

		Gas	Liquid-Gas	Solid-Gas
f11, f22	C-O stretch	15.483	-0.019	-0.019
f12	stretch-stretch	1.287	+0.054	+0.054
f33, f44	O-C-O bend	0.572	-0.004	-0.004
f55, f66, f 77	translation	0	0.136	0.174
f88, f99	libration	0	0.087	0.204
f68, f79	trans-lib	0	-0.028	-0.028

*Force constants f33, f44, f88, f99 have been divided by

r_e^2 ($r_e = 1.1615\text{\AA}$) and f68, f79 by r_e .

Table VIII

Shifts in the Internal Frequencies in the Isotopic
 CO_2 Molecules on Condensation (ν gas- ν solid)

	$\delta\nu_1$ (2352)		$\delta\nu_2$ (1285)		$\delta\nu_3$ (667)	
	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>
$^{12}\text{C}^{16}\text{O}_2$	6.8	6.03	(+0.5, +11.5)	-1.4	2.6	2.06
$^{13}\text{C}^{16}\text{O}_2$	3.5	5.87		-1.4	3.5	2.00
$^{12}\text{C}^{18}\text{O}_2$		5.94		-1.3		2.02

Table IX

Contributions to the Solid-Vapor Reduced Partition
 Function Ratios in the Isotopic CO_2 Molecules
 ($\text{C}^{16}\text{O}^{18}\text{O}/\text{C}^{16}\text{O}_2$)

	T^{-2}	T^{-1}	T
Translation	81.33	-0.061	
Libration	91.44	-0.050	-1.786×10^{-6}
Internal		-0.202	
$G(I, I')$		+0.011	
Total (1)	172.77	-0.302	-1.786×10^{-6}
Mean Square Torque Approximation	189.69	-	-

(1) = 1 molecule per unit cell.

Table X

Contributions to the Liquid-Vapor Reduced Partition Function Ratios
in the Isotopic CO₂ Molecules

	T^2			T^{-1}		
	(¹⁸ O ₂ / ¹⁶ O ₂)	(¹⁶ O ¹⁸ O/ ¹⁶ O ₂)	(¹³ C O ₂ / ¹² C O ₂)	(¹⁸ O ₂ / ¹⁶ O ₂)	(¹⁶ O ¹⁸ O/ ¹⁶ O ₂)	(¹³ C O ₂ / ¹² C O ₂)
Translation	113.52	54.86	24.87			
Rotation	50.20	27.62	5.44			
Internals				-0.076	-0.039	-.211
G(I, I')				+0.021	+0.011	
Total	163.72	82.48	30.31	-0.055	-0.028	-.211

Fig. 1. Plot of $T \ln(f_c/f_g)$ vs $10^3/T$ for $\Theta(C^{18}O_2/C^{16}O_2)$ (solid);

$\bullet (^{13}CO_2/^{12}CO_2)$ (solid)

$T \ln \alpha(C^{18}O^{16}O/C^{16}O_2)$ (liquid) Δ ;

$(^{13}CO_2/^{12}CO_2)$ (liquid) Δ

---- Calculated from F matrix set VI (1 molecule/unit
cell model).

— Calculated from the lattice dynamics of the real solid.

- - - - - Mean square torque calculations.

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