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Phase Equilibrium Isotope Effects in Molecular
Solids and Liquids.

Vapor Pressures of the Isotopic Nitrous
Oxide Molecules*

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ABSTRACT

The vapor pressures of three isotopic samples of N_2O enriched in ^{15}N and ^{18}O have been compared with normal N_2O over the temperature range $143^\circ - 219^\circ K$. Over the temperature range studied in the solid and in the liquid in the neighborhood of the triple point, the vapor pressures are in the sequence

$$^{14}N_2^{18}O > ^{14}N^{15}N^{18}O > ^{15}N^{14}N^{18}O > ^{14}N_2^{16}O.$$

The crossover phenomena have been observed for $^{15}N^{14}N^{18}O/^{14}N_2^{18}O$ at $207^\circ K$ and for $^{14}N^{15}N^{18}O/^{14}N_2^{18}O$ at 215° . The experimental data confirm hindered translation in both the solid and the liquid as well as the potential energy coupling of the translation and rotation found in CO_2 . Shifts in the internal stretching and bending modes on condensation lead to significant differences in the vapor pressures of the isomers $^{15}N^{14}N^{18}O$ and $^{14}N^{15}N^{18}O$. The latter has an abnormally large change in vapor pressure on melting compared with the other isotopic N_2O molecules studied. This is associated with the coupling of the internal bend coordinate with the translation in the solid, which vanishes in the liquid. The isotope effect in the high temperature liquid is explained in terms of an anharmonicity of the external motions in addition to the temperature dependence of the stretching force constant.

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. This model provides a good representation of the experimentally determined $\ln(fc/fg)$ for solid and liquid N_2O .

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 quite sensitive not only to the intermolecular interactions 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 have been obtained from the vapor pressure isotope effect studies of the rare gases¹⁻⁵. Studies on molecular liquids and solids have provided unique information about hindered rotation⁶⁻⁹, coupling of translation and rotation¹⁰⁻¹⁶, coupling of vibration with rotation^{8,17,18}, perturbation of internal rotation¹⁹ and vibrations¹⁸. The present work was undertaken to obtain information about molecular and intermolecular forces in solid and liquid N_2O by the vapor pressure isotope effect method. In view of the similarity of the many physical properties of N_2O with CO_2 , it was hoped that some of the unique features in the potential of solid and liquid CO_2 ¹⁶, e.g., the translation-libration coupling in the potential energy found by vapor pressure isotope effects, could be further studied by the asymmetric isotopic species which can be prepared in N_2O . Vapor pressure measurements were made on solid and liquid $^{14}N_2^{16}O$, $^{14}N_2^{18}O$, $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$.

II. Experimental

II. 1 Preparation and Purification of Samples

The manometric technique used for these vapor pressure measurements requires sizable quantities (300 cc to 400 cc NTP) of chemically pure and isotopically highly enriched samples. 0.8 liters of a gaseous $^{14}\text{N}_2^{16}\text{O}$ sample containing 93% ^{16}O were prepared by decomposition of ^{16}O enriched $\text{NH}_4\text{N}^{16}\text{O}_3$ which was obtained from the Weizmann Institute of Science. The decomposition reaction was carried out by the method described previously²⁰. About 10mm Hg of a helium gas was filled in the system in order to suppress sublimation of ammonium nitrate. The decomposition temperature was $210 \pm 10^\circ \text{C}$; temperature control was crude because of the large heat evolved in the reaction. The $^{14}\text{N}_2^{16}\text{O}$ formed after 1 ~ 2 percent decomposition was collected in a bulb after it was separated from the water formed in the decomposition. Continuous separation during the decomposition was effected by a series of cold traps. The $^{14}\text{N}_2^{16}\text{O}$ sample was derived from a Matheson C.P. grade sample. 0.5 liters each of 99.2% ^{15}N enriched $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and 99.0% ^{15}N enriched $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ samples were purchased from Prochem - British Oxygen Company, Ltd.

The isotope vapor pressure method at the sensitivity level used in this Laboratory requires samples with chemical impurities below the 10 ppm level. The main impurities in the crude samples were carbon dioxide with traces of water,

nitrogen and air. Preliminary purification was made by passing through a soda-lime bed followed by repeated trap to trap sublimation and passage through a multi-loop 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.

Further purification was made by the low temperature gas chromatographic process developed in this Laboratory. A preliminary experiment with a mixture of nitrous oxide and carbon dioxide showed satisfactory separation by this technique. In the purification, the chromatograph column, 0.21 in. i.d. stainless steel tubing, 10 ft long, was packed with ~30 g of chromsorb 102, 60/80 mesh, and wound in a spiral. Prior to each use, the column was activated by heating for 24 hr at 280° C under vacuum and then flushed for 24 hr at 280° C with helium gas which was passed through a charcoal bed immersed in a liquid nitrogen bath. The column^{was} then allowed to cool to -37.5° C, at which temperature it was maintained by anisole slush. 20 to 25 cc NTP of nitrous oxide sample was injected from the low temperature holding column at each run. Helium was used as a carrier gas. The effluent was passed through a thermal conductivity cell to monitor the separation. After the carbon dioxide passed through the thermal conductivity cell, the nitrous oxide was collected in a multi-loop trap immersed in liquid nitrogen. After being pumped at 77° K, the

purified sample was stored in a stainless steel lecture bottle. Final analysis of the sample by low temperature gas chromatography and mass spectrometry established the maximum total impurities in each of the samples below the 10 ppm level.

II. 2. Isotopic Analysis

The nitrous oxide samples were isotopically impure. The isotopic impurity levels of the four isotopic nitrous oxides used were required to correct the observed vapor pressure ratios. They were determined by mass spectroscopic analysis. The analysis was made with a Nuclide 6-60-RMS isotope mass spectrometer. The results of analysis are given in Table II. The procedure of determining the isotopic impurity levels was essentially the same as that used previously^{20,21}. In the determination, we assumed that the ^{17}O in the N_2^{16}O sample, the ^{17}O and ^{18}O in the $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ samples, and the ^{15}N in $^{14}\text{N}_2^{18}\text{O}$ sample were very close to their natural abundances. The isotopic composition of the samples used is given in Table II. For convenience in processing the experimental data, each sample was reduced to an effective four component isotopic mixture with the use of the rule of the mean²² and Raoul's law. Table III gives the effective mole fractions of the samples.

II. 3. Vapor Pressure Measurement

The vapor pressure measurements were made in the cryostat described previously²³. The sample of natural nitrous oxide served as a vapor pressure thermometer. Its pressure was read on a Texas Instrument quartz Bourdon gauge, which was calibrated in situ by a Ruska dead weight piston gauge, which had a National Bureau of Standards calibration. The temperature coefficient of the quartz gauge was determined directly by us. The precision of the absolute pressure measurement was ± 0.005 mm Hg. This sample of natural nitrous oxide was used as a reference pressure, P_N , against three other highly enriched samples. The pressure differences were measured with individual capacitance manometers (Datametrics, Inc., Model 511 Barocel Pressure Transducer) and read directly on a Hewlett-Packard 9830A computer which was interfaced through a Hewlett-Packard 3480B digital voltmeter. The quantity $\Delta P/P_N$ was measured with an absolute precision of about 5×10^{-5} as judged by the reproducibility of the measurements. The sample temperatures drifted less than $\pm 10^{-4}$ ° K during the course of a single measurement as judged by the response of the pressure gauge.

The sample temperatures were calculated from the vapor pressure data of Blue and Giaugue²⁴ in the range 143 - 184° K. In the temperature range 184 - 189° K, the P - T equation of

of Hoge²⁵ was used. At the triple point of N_2O the temperature scale of Hoge is higher than the Blue and GIAUQUE scale by $0.09^\circ K$. The vapor pressure data of Hoge for liquid N_2O were corrected to the Blue and GIAUQUE temperature scale. Finally all the data were corrected to the ice point $T = 273.15^\circ K$.²⁶ Above $189^\circ K$, temperatures were measured with a platinum resistance thermometer which was calibrated to $\pm 0.02^\circ K$ by us.

The vapor pressures of the pure isotopic species were derived from the pressure measurements and the isotopic composition of samples by the matrix equation:

$$\begin{pmatrix} P_N \\ \Delta P_i \\ \Delta P_j \\ \Delta P_k \end{pmatrix} = \begin{pmatrix} Y_1^N & Y_2^N & Y_3^N & Y_4^N \\ Y_1^N - Y_1^{E(i)} & Y_2^N - Y_2^{E(i)} & Y_3^N - Y_3^{E(i)} & Y_4^N - Y_4^{E(i)} \\ Y_1^N - Y_1^{E(j)} & Y_2^N - Y_2^{E(j)} & Y_3^N - Y_3^{E(j)} & Y_4^N - Y_4^{E(j)} \\ Y_1^N - Y_1^{E(k)} & Y_2^N - Y_2^{E(k)} & Y_3^N - Y_3^{E(k)} & Y_4^N - Y_4^{E(k)} \end{pmatrix} \begin{pmatrix} P_1^O \\ P_2^O \\ P_3^O \\ P_4^O \end{pmatrix} \quad (1)$$

where P_N is the measured vapor pressure of the normal N_2O sample, ΔP_i , ΔP_j and ΔP_k are the observed vapor pressure differences between normal and highly enriched " $^{14}N^{18}O$ ", " $^{15}N^{15}O$ " and " $^{15}N^{14}N^{16}O$ " samples respectively, P_1^O , P_2^O , P_3^O and P_4^O are the vapor pressures of four isotopically pure

$^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, respectively.

y_1^{N} , y_2^{N} ... $y_1^{\text{E}(i)}$, $y_2^{\text{E}(i)}$... $y_1^{\text{E}(j)}$, $y_2^{\text{E}(j)}$... $y_1^{\text{E}(k)}$,

$y_2^{\text{E}(k)}$... $y_4^{\text{E}(k)}$ are the effective four component mole

fractions. The superscripts N and E refer to normal and highly enriched samples, respectively.

III. Results

The measured quantities, T , P_{N} , and ΔP , are given in Table IV. Triple points of the four isotopic nitrous oxides have been calculated from the vapor pressure data and are given in Table V. Table IV also gives the logarithm of the reduced partition function ratios of the condensed phase referred to the ideal gas, $\ln(fc/fg)$ ($^{14}\text{N}_2^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$), $\ln(fc/fg)$ ($^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$), and $\ln(fc/fg)$ ($^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) which were derived from the measured quantities. We note that in the solid over the temperature range of our measurements $P_{^{14}\text{N}_2^{16}\text{O}} > P_{^{14}\text{N}^{15}\text{N}^{16}\text{O}} > P_{^{15}\text{N}^{14}\text{N}^{16}\text{O}} > P_{^{14}\text{N}_2^{18}\text{O}}$, while in the liquid crossover phenomena are observed.

The reduced partition function ratio is related to the vapor pressure ratio by the equation^{1, 27}

$$\ln(fc/fg) = [1 + P(B_0 - V_c/RT)] \ln(P'/P), \quad (2)$$

where V_c is the molal volume of the condensed phase and B_0 is the second virial coefficient when the equation of state is written in the form

$$PV/RT = 1 + B_0 \cdot P + \dots$$

The temperature dependence of B_0 is ²⁸

$$B_0(\text{atm}^{-1}) = \frac{0.39001}{T} - \frac{68.391}{T^2} + \frac{4.8049 \times 10^4}{T^3} - \frac{4.7709 \times 10^9}{T^5} + \frac{3.7473 \times 10^{13}}{T^7} \quad (3)$$

The reduced partition function ratios for the solid isotopic N_2O molecules were fitted to equations of the form

$$\ln(f_c/f_g) = A/T^2 - B/T + CT \quad (4)$$

The parameters A , B and C are given in Table VI, VII and VIII for $^{14}N_2^{18}O/^{14}N_2^{16}O$, $^{15}N^{14}N^{16}O/^{14}N_2^{16}O$ and $^{14}N^{15}N^{16}O/^{14}N_2^{16}O$, respectively. Within the framework of the statistical mechanical theory of condensed phase isotope effects²⁷ extended to include anharmonic terms^{2, 16, 29, 30}, the quantities A , B , and C have the following physical meaning: 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 internal vibration from the gas to the condensed

phase, the anharmonicity of libration and translation in the condensed phase and the correction to the non-classical rotation in the gas phase; C is a librational anharmonic effect. In the case of N_2O , u (bending) $= h\nu_{\text{bend}}/kT$ is less than 2π over the temperature range of our measurements; thus the shift in the internal bending vibrations from the gas to the condensed phases contributes to both A and B of Eq. (4).

A plot of $T^2 \ln(f_c/f_g)$ vs. T is given in Fig. 1 for the $^{14}N_2^{18}O/^{14}N_2^{16}O$, $^{14}N^{15}N^{16}O/^{14}N_2^{16}O$ and $^{15}N^{14}N^{16}O/^{14}N_2^{16}O$ ratios of solid and liquid nitrous oxides. Fig. 1 also includes values derived from the isotope distillation experiments and vapor pressure measurements in the liquid by Bigeleisen and Ribnikar⁶ and Clusius and Schleich³¹, respectively. The present measurements fully confirm the measurements made on the three isotopic species by the distillation technique. While the measurements of Clusius and Schleich are in good agreement with the present data, they do not have the accuracy claimed by the authors. It is to be noted that $\ln(f_s/f_l)(^{14}N^{15}N^{16}O) / (^{14}N_2^{16}O)$ at the triple point is especially large when compared to the similar quantities for $(^{15}N^{14}N^{16}O/^{14}N_2^{16}O)$ and $(^{14}N_2^{18}O/^{14}N_2^{16}O)$.

IV. Discussion

As an aid to the understanding of the absolute value of the reduced partition function ratio of the condensed phase referred to the ideal gas, $\ln(fc/fg)$, we made a calculation of $\ln(fc/fg)$ by the Stern, Van Hook and Wolfsberg cell model¹⁸. The model has the capability of describing in a quantitative way hindered translation and rotation, the coupling of translation and rotation with one another and with internal coordinates. It uses the same basic set of external coordinates for all isotopic species and an isotope independent F matrix, consistent with the Born-Oppenheimer approximation.

The study of carbon dioxide^{16,30} shows that the single molecule per unit cell model is an excellent approximation to the complete calculation of the real solid with four molecules per unit cell. In this paper we present the result of a calculation of $\ln(fc/fg)$ made for both the solid and liquid nitrous oxides with a single molecule in a unit cell. The external coordinates of $^{14}\text{N}_2^{16}\text{O}$ were chosen as the basis coordinates for all the external modes, i.e., translation and rotation of all isotopic N_2O molecules. The method of calculation assumes that $\ln(fc/fg)$ can be calculated in the harmonic oscillator approximation for both solid and gas phases, but that the F matrix elements associated with translation and rotation are temperature dependent.

Within the harmonic oscillator approximation, $\ln(fc/fg)$ is given by²⁷

$$\begin{aligned} \ln(fc/fg) = & \sum_{\text{ext}} [\lnb(u_i')_c - \lnb(u_i)_c] \\ & + \sum_{\text{int}} [\lnb(u_i')_c - \lnb(u_i)_c - \lnb(u_i')_g + \lnb(u_i)_g] \\ & - G(I, I') \end{aligned} \quad (5)$$

where $\lnb(u) = -\ln u + u/2 + \ln(1 - e^{-u})$, $u_i = hv_i/kT$, the prime denotes the lighter isotope and the subscripts c and g refer to the condensed and gas phases, respectively. For the external modes, the $u^2/24$ law is a good approximation to $\lnb(u)$, while $\lnb(u_i)_c - \lnb(u_i)_g$ reduces to $(1/2)(u_{ic} - u_{ig})$ for the stretching vibrations since $u_{\text{stretch}} > 2\pi$. For the bending mode, $\lnb(u)$ was calculated exactly and then fitted by the following least square equation

$$\lnb(u)_{\text{bend}} = au^2 + bu + c$$

where $a = 0.014903$, $b = 0.15806$ and $c = -0.27904$. A and B in Eq. (4) are therefore given by

$$\begin{aligned} A = & \frac{1}{24}(h/k)^2 \sum_{\text{ext}} (v_i'^2 - v_i^2)_c \\ & + a(h/k)^2 \sum_{\text{bend}} [(v_i'^2 - v_i^2)_c - (v_i'^2 - v_i^2)_g], \end{aligned} \quad (6)$$

$$B = (h/2k) \sum_{\text{stretch}} [(\nu'_i - \nu_i)_g - (\nu'_i - \nu_i)_c] \\ + b(h/2k) \sum_{\text{bend}} [(\nu'_i - \nu_i)_g - (\nu'_i - \nu_i)_c] + G(I, I') \quad (7)$$

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

$$G(I, I') \approx (hc/3k) (B_e - B'_e) \quad (8)$$

where B_e is the rotational constant in wave numbers.

If one applies an anharmonic correction to Eq'ns (6,7), then B in Eq. (4) is¹⁶

$$B = B(7) + A_{\text{tr}}^0 \cdot \alpha_{\text{tr}} + A_{\text{rot}}^0 \cdot \alpha_{\text{rot}} \quad (9)$$

where $B(7)$ is given by Eq. (7) and α_{tr} and α_{rot} are defined by Eq'ns (10) and (11), respectively.

$$A_{\text{tr}} = A_{\text{tr}}^0 (1 - \alpha_{\text{tr}} \cdot T) \quad (10)$$

$$A_{\text{rot}} = A_{\text{rot}}^0 (1 - \alpha_{\text{rot}} \cdot T - \beta_{\text{rot}} T^3) \quad (11)$$

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

$$\langle v^2 \rangle = \langle v^2 \rangle_{Ar}^0 (1 - 1.956 \times 10^{-3} T)$$

lead to a value of 8.935×10^{-4} for $\alpha_{tr}(N_2O)$. The anharmonic rotational constants α_{rot} and β_{rot} were determined from the temperature dependence of the Raman spectral data of solid N_2O of Cahill and Leroi³², and Anderson and Sun³³. A least square fit was made to their data to get α_{rot} and β_{rot} through the relation

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

Thus we find for solid N_2O

$$A_{rot} = A_{rot}^0(1 - 6.831 \times 10^{-4} T - 1.340 \times 10^{-8} T^3) .$$

The $^{14}N^{15}N^{16}O/^{14}N_2^{16}O$ ratio has almost zero rotational effect except from coupling terms because the central nitrogen is virtually at the center of mass of the molecule (the ratio of the moments of inertia of $^{14}N^{15}N^{16}O/^{14}N_2^{16}O$ was determined by microwave spectroscopy³⁴ to be 1.000068). The least square value of A for the $^{14}N^{15}N^{16}O/^{14}N_2^{16}O$ ratio is much bigger than

that calculated with $\underline{F}$ matrix without off-diagonal elements between externals and internals. The derivatives of A and B terms with respect to $\underline{F}$ matrix elements serve as a guide as to which $\underline{F}$ matrix element affects these terms in the reduced partition function ratios of the individual isotopic nitrous oxides. Only the coupling of the bending vibration with the external modes gives a significant contribution to the A term of the $^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ ratio, while it does not affect the other two isotopic ratios significantly. After a preliminary estimate of the translational and rotational effects, the contribution of bending vibration was determined from the ($^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) data. Since present spectroscopic information is inadequate to calculate the contributions of the internal vibrations to the B-term in Eq. (4), the experimentally determined $\ln(fc/fg)$ was finally used to derive the total shift in the stretching force constants.

Solid N_2O has four molecules in the unit cell. The following relationships suffice to complete the one molecule per unit cell model.

$$8v_{\text{rot}}^2(1) = \sum^8 v_{\text{lib}}^2 \quad (12)$$

$$12v_{\text{tr}}^2(1) = \sum^9 v_{\text{tr}}^2 \quad (13)$$

In Eq'ns (12) and (13), ν_{lib} and ν_{tr} are the spectroscopically determined librational and translational frequencies, respectively. The notation $\nu_{rot}^2(1)$ and $\nu_{tr}^2(1)$ defines two sets of Einstein frequencies for the rotation and translation in the one molecule per unit cell model. The Einstein frequencies for $^{14}\text{N}_2^{16}\text{O}$ are 99.1 cm^{-1} and 78.6 cm^{-1} for $\nu_{rot}(1)$ and $\nu_{tr}(1)$, respectively. These frequencies lead to values of $0.182 \text{ md/\AA}$ for $f_{rot} = f_{55} = f_{88}$ and $0.160 \text{ md/\AA}$ for $f_{tr} = f_{33} = f_{66} = f_{99}$. Within the one molecule per unit cell model a translation-libration $\underline{F}$ matrix element, $f_{56} = f_{89}$, is necessary to fit the ratios of $^{14}\text{N}_2^{18}\text{O}/^{14}\text{N}_2^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$, while the interaction force constants of bending vibration with libration and translation, $f_{45} = f_{78}$ and $f_{46} = f_{79}$, are necessary to interpret the $^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ ratio. The $\underline{G}$ matrix elements were derived according to the formulation given by Stern, Van Hook and Wolfsberg¹⁸. The $\underline{F}$ matrices for the gas and solid N_2O are given in Table IX. For comparison, Table IX also includes the $\underline{F}$ matrix for the solid CO_2 ¹⁶ which is similar to N_2O in many aspects: they are isoelectronic and have a small or zero dipole moment, a reasonably large negative quadrupole moment, identical nuclear frameworks and a similar crystal structure. We note that the translation-libration interaction force constant of the solid N_2O derived from spectroscopic data combined with experimentally determined isotopic vapor pressure data is quite similar with that of the solid CO_2 .

The contributions of translation, libration, internal vibration and non-classical rotation in the gas phase to the various terms A/T^2 , B/T and CT in Eq. (4) are tabulated separately in Tables VI, VII and VIII for $\ln(fc/fg)$ ($^{14}\text{N}_2^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$), ($^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) and ($^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$), respectively. It may be seen that hindered translation and hindered rotation give the dominant contribution to $\ln(fc/fg)$ for $^{14}\text{N}_2^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$. On the other hand the contributions of the coupling of the bending vibration with the external modes and the hindered translation dominate the condensed phase isotope effect of $^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ in the solid.

The translation-libration F matrix coupling constant, $-0.026 \text{ mdyne } \text{\AA}^{-1}$, introduces a large interaction between the translational and rotational coordinates. The eigenvectors are significantly different from the basis coordinates. The entries in Tables VI, VII, and XI labelled "translation" and "libration" are not to be taken literally since these are not pure modes. The significant entry is the sum of "translation" plus "libration".

The total B term was adjusted to fit the experimental B terms. The significant comparison on the B term is in Table X where we see that the frequency shifts from gas to solid calculated from the isotopic vapor pressure data

are in reasonable agreement with the spectroscopic observations^{33, 35, 38, 39}. Since they are calculated from the F , G 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 least square isotopic vapor pressure measurements is of the same order of magnitude as that calculated from the Raman data.

Our experimental data on the four isotopic N_2O species cover the liquid range from the triple points (182° K) to 219° K. The values of the logarithm of the solid to liquid partition function ratios at the triple point of the substituted N_2O molecules compared with $^{14}N_2^{16}O$ are 1.75 for both ^{15}N and ^{18}O end atom substitution but 2.91 for ^{15}N central atom substitution. To understand the large difference in central atom isotope effect compared with end atom isotope effect on melting, we have made model calculations of $\ln(f_l/f_g)$ of the various isotopic species in the liquid in the neighborhood of the triple point. We shall use the simple cell model of the liquid and assume the internal F matrix elements are the same in the liquid in the vicinity of the triple point as those in the gas. We shall derive the harmonic values of A/T^2 associated with translation and rotation. In conformity with the results on CO_2 ,¹⁶ we shall assume the same translation-rotation F matrix coupling in the liquid as in the solid.

Previous work on the rare gases show that

$$(A_1 / A_s)_{\text{trans}} = (V_s / V_l) \quad (14)$$

where V is the molal volume and the subscripts l and s refer to liquid and solid, respectively. The molal volumes of the solid and liquid N_2O at the triple point are $29.73 \text{ cc mole}^{-1}$ and $35.80 \text{ cc mole}^{-1}$, respectively³⁶. This leads to a value of $0.134 \text{ md/\AA}$ for the harmonic (182°K) diagonal force constant, $f_{\text{tr}} = f_{33} = f_{66} = f_{99}$ of the liquid. For the rotation, we shall use the principle of corresponding states for the effective torsional oscillation amplitude, $R < \theta^2 >^{1/2}$, which has been found experimentally for diatomic and linear triatomic molecules³⁷. The relationship

$$R < \theta^2 >^{1/2} / T^{*1/2} = 0.34 \pm 0.03 \text{ \AA}$$

gives a value of 81 rad^{-2} for the mean square torque on a N_2O molecule, $\langle (OU/kT)^2 \rangle$, in the liquid at the triple point and leads to a value of $0.072 \text{ md/\AA}$ for the rotational force constant, $f_{\text{rot}} = f_{55} = f_{88}$. In arriving at f_{rot} we define $T^* = T/T_c$ (critical point). R is the length of the molecular axis and θ is measured in radians. We are now in a position to calculate the $\ln(f_c/f_g)_{\text{liq}}$ at the triple point. The contributions of

translation, rotation and internal vibration to $T^2 \ln(fc/fg)_1$ have been calculated through the F G matrices and are given in Table XI, where they are compared with the experimental data. The agreement between theory and experiment is remarkably good. This indicates that the contributions from changes in the internal F matrix elements from the gas to the liquid near triple point is negligibly small. Our calculations assumed that the force constants of the internal modes were the same as the value of gas phase. The change from a perturbed to an unperturbed bending vibration by the external modes explains the large isotope effect on melting for the $^{15}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ ratio. It may be seen that the onset of much freer 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.

In the liquid over the temperature range of our experiment, the temperature dependence of $\ln(fc/fg)$ ($^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) is quite different from the other two ratios, while the temperature dependence of $\ln(fc/fg)$ ($^{14}\text{N}_2^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) and ($^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$) are very similar to one another. It is obvious that the temperature dependence of $T^2 \ln(fl/fg)$ is to be associated with the change in the N-N and N-O stretching constants in the liquid as a function of the temperature. We shall use the following simplified model, based on the success of the calculation of $\ln(fl/fg)$ in the liquid at the

triple point, for the calculation of the temperature dependence of $\ln(f_l/f_g)$ for the various isotopic species. The observed temperature dependence of $\ln(f_l/f_g)$ for $(^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O})$ and the absence of any rotational contribution to the latter leads us to postulate that to first approximation all of the temperature dependence of $T^2(\ln(f_l/f_g))$ is associated with a temperature dependent B , $B(T)$, in Eq. 4. The anharmonic contributions of the external motions have been calculated from the temperature dependence of the frequencies obtained by Raman and IR spectroscopy. The translational and rotational force constants in the liquid are given by

$$F_{tt} = F_{tt}(182^\circ\text{K}) \left\{ 1 - 1.39692 \times 10^{-3}T + 1.156743 \left(1 - \frac{T}{309.55} \right)^{1/3} \right\} \times 0.62284$$

$$F_{rr} = F_{rr}(182^\circ\text{K}) \left\{ 1 - 1.39692 \times 10^{-3}T + 1.156743 \left(1 - \frac{T}{309.55} \right)^{1/3} \right\}^{3.21} \times 0.21875$$

The three isotopic pairs then suffice to determine the temperature dependence of the three stretching force constants

$f_{11} = f_{\text{N-N}}$, $f_{\text{N-O}} = f_{22}$, and f_{12} . A least square fit from the experimental vapor pressure data gives:

$$\begin{aligned}
 f_{11} = & 18.480 - 7.275 \times 10^{-4} (T - T_{tr}) \\
 & + 1.795 \times 10^{-4} (T - T_{tr})^2 \\
 & - 6.777 \times 10^{-6} (T - T_{tr})^3
 \end{aligned} \tag{16}$$

$$\begin{aligned}
 f_{22} = & 11.830 + 7.579 \times 10^{-4} (T - T_{tr}) \\
 & - 1.761 \times 10^{-5} (T - T_{tr})^2 \\
 & - 2.923 \times 10^{-6} (T - T_{tr})^3
 \end{aligned} \tag{17}$$

$$\begin{aligned}
 f_{12} = & 1.130 - 1.88 \times 10^{-3} (T - T_{tr}) \\
 & - 7.91 \times 10^{-5} (T - T_{tr})^2 \\
 & + 7.56 \times 10^{-7} (T - T_{tr})^3
 \end{aligned} \tag{18}$$

where T_{tr} is the triple point temperature. While the temperature coefficient of f_{12} is comparable to those of f_{11} and f_{22} , the temperature dependence of f_{12} contributes little to the temperature coefficients of the B terms for the three isotopic species compared with $^{14}\text{N}_2^{16}\text{O}$. The temperature dependence of the N-N and N-O stretching force constants, f_{11} and f_{22} respectively, explains the trend of $\ln(f_1/f_g)$.

The main difference between the N_2O and CO_2 systems is the internal frequency shifts during the condensation. All the diagonal internal force constants are larger in solid N_2O than in the gas. In liquid N_2O in the neighborhood of the triple point, the internal force constants are almost the same as those of the gas phase. As the temperature increases, the internal force constants of the liquid decrease. For the CO_2 system, all the diagonal elements of the internal force constants in the condensed phases are smaller than those in the gas phase. Not only are the diagonal external F matrix elements for both solid and liquid N_2O very close to the respective values in CO_2 , but the more extensive N_2O data yield an off diagonal translation-libration F matrix element in good agreement with that derived from the sparse CO_2 results. It is possible that some of the internal shift in CO_2 bending force constant between solid and gas may in fact be a non zero off diagonal bending-translational force constant established by the N_2O data.

The crossover phenomena have been observed for the first time for heavy atom vapor pressure isotope effects. For ($^{15}N^{14}N^{16}O/^{14}N_2^{16}O$) it occurs at $207^\circ K$ and for ($^{14}N^{15}N^{16}O/^{14}N_2^{16}O$) at $215^\circ K$. We have estimated the crossover temperatures to be $222^\circ K$ and $228^\circ K$ for ($^{14}N_2^{18}O/^{14}N_2^{16}O$) and ($^{15}N^{14}N^{16}O/^{14}N_2^{16}O$), respectively, by extrapolation of Eq'ns (16), (17) and (18).

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Fig. 1. Plot of $T^2 \ln(f_c/f_g)$ vs T for the solid and liquid N_2O .

$^{14}N_2^{16}O/^{14}N_2^{15}O$; -o- (present work), $\odot$ (Bigeleisen and Ribnikar).

$^{15}N^{14}N^{16}O/^{14}N_2^{15}O$; - $\odot$ - (present work), $\odot$ (Bigeleisen and Ribnikar), $\times$ (Clusius and Schleich).

$^{14}N^{15}N^{16}O/^{14}N_2^{16}O$; - $\odot$ - (present work), $\odot$ (Bigeleisen and Ribnikar)..

Table I. Isotopic Analysis of N₂O Samples

Ratio found	Sample			
	" ¹⁴ N ₂ ¹⁶ O"	" ¹⁴ N ¹⁵ N ¹⁶ O"	" ¹⁵ N ¹⁴ N ¹⁶ O"	" ¹⁴ N ₂ ¹⁸ O"
45/44	7.865 x 10 ⁻³			
46/44	2.145 x 10 ⁻³			
44/45		5.300 x 10 ⁻³	7.432 x 10 ⁻³	
46/45		6.575 x 10 ⁻³	5.046 x 10 ⁻³	
47/45		2.088 x 10 ⁻³	2.076 x 10 ⁻³	
48/45		1.250 x 10 ⁻⁵	1.147 x 10 ⁻⁵	
44/46				6.313 x 10 ⁻²
45/46				4.446 x 10 ⁻³
47/46				7.465 x 10 ⁻³
48/46				1.531 x 10 ⁻⁵
30/31	254.9			
30/33				17.52

Table II. Isotopic Composition of the Nitrous Oxide
Samples (in percent)

Species	Sample			
	" $^{14}\text{N}_2^{16}\text{O}$ "	" $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ "	" $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ "	" $^{14}\text{N}_2^{18}\text{O}$ "
$^{14}\text{N}_2^{16}\text{O}$	99.00 ₉	0.52 ₃	0.73 ₃	5.87 ₃
$^{14}\text{N}_2^{17}\text{O}$	0.03 ₇	-	-	0.37 ₀
$^{14}\text{N}_2^{18}\text{O}$	0.21 ₁	0.00 ₁	0.00 ₁	93.01 ₉
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	0.37 ₁	98.62 ₂	0.00 ₃	0.02 ₂
$^{14}\text{N}^{15}\text{N}^{17}\text{O}$	-	0.03 ₇	-	0.00 ₁
$^{14}\text{N}^{15}\text{N}^{18}\text{O}$	-	0.02 ₀	-	0.34 ₅
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	0.37 ₁	0.00 ₃	98.56 ₂	0.02 ₂
$^{15}\text{N}^{14}\text{N}^{17}\text{O}$	-	-	0.03 ₇	0.00 ₁
$^{15}\text{N}^{14}\text{N}^{18}\text{O}$	-	-	0.20 ₂	0.34 ₅
$^{15}\text{N}_2^{16}\text{O}$	0.00 ₁	0.61 ₁	0.46 ₁	-
$^{15}\text{N}_2^{17}\text{O}$	-	-	-	-
$\text{N}_2 \text{ O}$	-	0.00 ₁	0.00 ₁	0.00 ₁

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

Sample	$^{14}\text{N}_2^{16}\text{O}$	$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	$^{14}\text{N}_2^{18}\text{O}$
" $^{14}\text{N}_2^{16}\text{O}$ "	99.03	0.37	0.37	0.23
" $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ "	-0.31	99.47	0.62	0.22
" $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ "	0.05	0.47	99.26	0.22
" $^{14}\text{N}_2^{18}\text{O}$ "	5.36	0.37	0.37	93.90

Table IV. Observed Vapor Pressures and Reduced
Partition Function Ratios for $^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$,
 $^{15}\text{N}^{14}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$ and $^{14}\text{N}_2^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$.

T(°K)	P_N^a	A^a	B^a	C^a	D^a	E^a	F^a
143.88	9.82	3.90	5.13	6.17	3.96	5.20	6.59
145.07	11.58	3.85	5.06	6.07	3.91	5.13	6.49
145.85	12.89	3.84	5.00	6.00	3.89	5.06	6.41
145.87	12.92	3.84	5.02	6.00	3.89	5.09	6.42
147.10	15.25	3.80	4.91	5.90	3.85	4.98	6.31
147.75	16.61	3.81	4.89	5.86	3.86	4.96	6.26
150.12	22.60	3.66	4.74	5.69	3.70	4.80	6.09
151.12	25.68	3.62	4.72	5.60	3.66	4.78	5.99
152.85	31.87	3.47	4.59	5.49	3.51	4.65	5.87
154.58	39.30	3.53	4.45	5.37	3.57	4.51	5.75
155.68	44.90	3.46	4.37	5.29	3.50	4.43	5.66
155.69	44.90	3.47	4.39	5.30	3.50	4.45	5.67
156.70	50.66	3.42	4.33	5.22	3.45	4.39	5.59
157.93	58.40	3.39	4.28	5.15	3.42	4.33	5.51
158.10	59.60	3.29	4.16	5.07	3.32	4.22	5.43
159.24	67.90	3.30	4.16	5.04	3.33	4.21	5.39
160.48	78.04	3.28	4.12	4.96	3.30	4.17	5.32
161.88	91.12	3.24	4.06	4.88	3.27	4.11	5.22
163.03	103.21	3.19	4.01	4.81	3.22	4.06	5.14
164.52	121.07	3.14	3.91	4.71	3.17	3.95	5.03
166.05	142.16	3.08	3.83	4.63	3.11	3.87	4.95
168.25	178.34	3.01	3.76	4.54	3.04	3.80	4.85
168.26	178.42	2.91	3.63	4.49	2.93	3.67	4.79
168.27	178.73	2.93	3.65	4.47	2.95	3.69	4.77
169.74	206.95	2.91	3.58	4.41	2.93	3.62	4.71

169,75	207,30	3,00	3,71	4,45	3,02	3,75	4,76
169,82	208,70	3,01	3,74	4,48	3,03	3,78	4,78
171,04	235,46	2,90	3,58	4,36	2,91	3,61	4,66
171,61	248,83	2,92	3,62	4,35	2,94	3,66	4,64
172,88	281,21	2,85	3,55	4,27	2,87	3,58	4,55
173,17	289,08	2,80	3,48	4,22	2,81	3,51	4,49
173,31	293,19	2,77	3,47	4,19	2,79	3,50	4,46
174,37	324,08	2,67	3,45	4,24	2,68	3,48	4,52
176,25	385,99	2,77	3,39	4,09	2,78	3,42	4,36
176,32	388,48	2,78	3,39	4,11	2,79	3,41	4,38
177,73	441,77	2,76	3,36	4,05	2,77	3,38	4,31
177,76	443,06	2,70	3,40	4,01	2,71	3,42	4,26
178,90	490,98	2,67	3,33	4,00	2,68	3,36	4,25
179,29	508,55	2,70	3,31	3,99	2,70	3,33	4,24
179,52	519,09	2,75	3,39	4,01	2,76	3,41	4,26
180,14	548,16	2,66	3,26	3,96	2,67	3,28	4,21
180,85	583,33	2,63	3,19	3,86	2,63	3,21	4,10
181,19	600,77	2,53	3,18	3,85	2,54	3,19	4,09
181,20	601,13	2,64	3,17	3,82	2,64	3,18	4,06
181,37	610,05	2,59	3,11	3,81	2,59	3,13	4,04
181,41	612,03	2,60	3,21	3,89	2,60	3,22	4,13
181,66	625,55	2,65	3,23	3,89	2,65	3,25	4,13
181,86	636,46	2,69	3,22	3,88	2,69	3,24	4,11
181,95	641,66	2,69	3,22	3,85	2,69	3,23	4,09
182,14	651,86	2,70	3,23	3,90	2,71	3,24	4,14

182.21	656.22	2.61	3.17	3.78	2.61	3.18	4.01
182.21	656.26	2.58	3.22	3.78	2.58	3.24	4.01
182.22	656.32	2.61	3.21	3.82	2.61	3.22	4.05
182.22	656.80	2.58	3.23	3.79	2.58	3.24	4.02
182.24	657.88	2.58	3.10	3.77	2.58	3.11	4.01
182.25	658.10	2.52	3.08	3.76	2.52	3.09	3.99
182.26	658.78	2.42	2.97	3.69	2.43	2.98	3.91
182.26	658.77	2.54	3.06	3.73	2.54	3.07	3.96
182.26	658.95	2.54	3.06	3.72	2.54	3.07	3.95
182.26	658.99	2.50	3.04	3.74	2.51	3.06	3.97
182.26	659.00	2.48	3.02	3.69	2.49	3.03	3.91
182.26	659.02	2.48	3.01	3.68	2.48	3.02	3.91
182.26	659.12	2.47	2.96	3.65	2.47	2.98	3.88
182.26	659.13	2.24	2.77	3.49	2.24	2.79	3.70
182.27	659.23	2.43	2.95	3.64	2.44	2.97	3.86
182.27	659.37	2.34	2.81	3.49	2.34	2.82	3.71
182.27	659.40	2.07	2.75	3.50	2.07	2.76	3.72
182.27	659.41	2.05	2.72	3.43	2.05	2.74	3.64
182.27	659.41	2.05	2.70	3.36	2.05	2.71	3.56
182.27	659.49	2.23	2.72	3.41	2.23	2.74	3.62
182.28	659.62	1.97	2.51	3.27	1.98	2.52	3.47
182.29	660.03	1.86	2.47	3.19	1.86	2.48	3.39
182.29	660.22	1.74	2.44	3.12	1.74	2.45	3.31
182.29	660.30	1.56	2.27	3.01	1.56	2.28	3.20
182.31	660.79	1.45	1.94	2.59	1.45	1.95	2.76

182.31	660.81	1.23	1.87	2.60	1.24	1.88	2.76
182.31	660.97	1.35	1.87	2.51	1.35	1.88	2.66
182.31	660.97	1.25	1.84	2.42	1.25	1.85	2.57
182.31	661.00	1.28	1.85	2.47	1.29	1.86	2.62
182.31	661.06	1.26	1.84	2.46	1.27	1.85	2.61
182.31	661.09	1.24	1.83	2.44	1.24	1.84	2.59
182.31	661.10	1.24	1.82	2.44	1.25	1.83	2.59
182.31	661.12	1.22	1.81	2.43	1.22	1.82	2.58
182.31	661.12	1.22	1.80	2.42	1.23	1.81	2.57
182.31	661.13	1.20	2.03	2.87	1.21	2.04	3.04
182.31	661.13	1.19	2.01	2.83	1.19	2.02	3.00
182.31	661.13	1.18	2.00	2.81	1.19	2.01	2.98
182.31	661.14	1.22	1.80	2.41	1.22	1.81	2.56
182.31	661.14	1.20	1.79	2.40	1.20	1.80	2.55
182.31	661.14	1.17	2.01	2.76	1.18	2.02	2.93
182.31	661.15	1.20	1.78	2.41	1.20	1.79	2.56
182.31	661.15	1.20	1.79	2.40	1.21	1.80	2.55
182.31	661.15	1.20	1.78	2.40	1.20	1.79	2.55
182.31	661.15	1.20	1.79	2.40	1.20	1.80	2.55
182.31	661.16	1.16	2.01	2.73	1.16	2.02	2.89
182.31	661.16	1.20	1.78	2.40	1.20	1.79	2.54
182.31	661.16	1.19	1.78	2.39	1.20	1.80	2.54
182.31	661.16	1.19	1.79	2.40	1.19	1.80	2.55
182.31	661.17	1.15	2.01	2.69	1.15	2.02	2.85
182.31	661.17	1.15	2.01	2.69	1.16	2.02	2.86

182,31	661,10	1,16	1,84	2,36	1,16	1,85	2,51
182,32	661,21	1,14	2,01	2,68	1,15	2,02	2,85
182,32	661,22	1,16	1,78	2,36	1,16	1,79	2,51
182,32	661,31	1,13	1,77	2,32	1,13	1,78	2,46
182,32	661,33	1,11	1,96	2,67	1,11	1,98	2,84
182,32	661,36	0,91	1,89	2,26	0,92	1,90	2,40
182,32	661,40	1,06	1,95	2,60	1,07	1,96	2,76
182,32	661,40	1,04	1,94	2,56	1,05	1,95	2,71
182,32	661,43	1,03	1,94	2,50	1,03	1,95	2,65
182,32	661,51	1,01	1,92	2,46	1,02	1,93	2,61
182,32	661,51	1,04	1,78	2,24	1,04	1,80	2,38
182,32	661,52	0,96	1,91	2,30	0,96	1,92	2,40
182,32	661,52	0,96	1,91	2,29	0,96	1,92	2,43
182,32	661,50	0,96	1,91	2,28	0,96	1,93	2,42
182,32	661,49	0,98	1,83	2,29	0,98	1,84	2,43
182,32	661,52	0,95	1,84	2,18	0,95	1,85	2,32
182,32	661,58	1,00	1,79	2,20	1,01	1,80	2,34
182,33	661,59	0,98	1,92	2,41	0,99	1,93	2,56
182,33	661,59	0,98	1,91	2,42	0,98	1,92	2,57
182,33	661,62	0,97	1,80	2,18	0,97	1,81	2,32
182,33	661,62	0,94	1,80	2,16	0,95	1,81	2,29
182,33	661,64	0,95	1,80	2,18	0,96	1,81	2,31
182,33	661,67	0,94	1,80	2,15	0,94	1,81	2,29
182,33	661,62	0,92	1,85	2,18	0,92	1,86	2,31
182,33	661,67	0,93	1,81	2,16	0,93	1,82	2,29

182.33	661.69	0.92	1.81	2.16	0.93	1.82	2.29
182.33	661.72	0.93	1.81	2.17	0.93	1.82	2.30
182.33	661.70	0.90	1.85	2.18	0.90	1.86	2.31
182.33	661.79	0.93	1.81	2.16	0.94	1.82	2.29
182.33	661.82	0.92	1.81	2.16	0.92	1.82	2.29
182.33	661.83	0.91	1.81	2.16	0.91	1.82	2.29
182.33	661.84	0.89	1.81	2.16	0.90	1.82	2.29
182.33	661.84	0.89	1.81	2.16	0.89	1.82	2.29
182.33	661.85	0.88	1.81	2.16	0.88	1.82	2.29
182.33	661.86	0.88	1.81	2.15	0.88	1.82	2.29
182.33	661.89	0.88	1.81	2.15	0.88	1.82	2.29
182.33	661.93	0.89	1.81	2.15	0.89	1.82	2.29
182.33	661.95	0.91	1.81	2.15	0.91	1.82	2.29
182.34	662.03	0.88	1.81	2.15	0.88	1.82	2.29
182.34	662.10	0.87	1.81	2.15	0.88	1.82	2.29
182.34	662.08	0.88	1.86	2.17	0.89	1.87	2.30
182.34	662.15	0.87	1.81	2.15	0.87	1.82	2.29
182.34	662.20	0.86	1.81	2.15	0.87	1.83	2.29
182.34	662.25	0.86	1.81	2.15	0.86	1.83	2.29
182.34	662.29	0.85	1.81	2.15	0.86	1.83	2.29
182.34	662.27	0.88	1.86	2.17	0.88	1.87	2.30
182.34	662.37	0.85	1.82	2.15	0.86	1.83	2.28
182.35	662.41	0.85	1.82	2.15	0.85	1.83	2.28
182.35	662.52	0.85	1.82	2.15	0.85	1.83	2.28
182.35	662.64	0.85	1.82	2.15	0.85	1.83	2.28

182.35	662.66	0.88	1.86	2.17	0.89	1.87	2.30
182.36	663.21	0.88	1.86	2.17	0.88	1.87	2.30
182.38	663.87	0.88	1.85	2.16	0.88	1.86	2.29
182.40	664.52	0.87	1.85	2.13	0.88	1.86	2.27
182.40	664.55	0.87	1.85	2.13	0.88	1.86	2.27
182.40	664.77	0.88	1.86	2.16	0.88	1.87	2.30
182.43	665.78	0.88	1.86	2.16	0.88	1.87	2.29
182.45	666.78	0.87	1.85	2.15	0.88	1.86	2.28
182.48	668.10	0.87	1.85	2.15	0.88	1.86	2.28
182.51	669.11	0.87	1.85	2.15	0.88	1.86	2.28
182.53	669.82	0.87	1.85	2.15	0.88	1.86	2.29
182.53	669.96	0.86	1.83	2.11	0.86	1.84	2.25
182.56	671.36	0.87	1.85	2.14	0.87	1.86	2.27
182.57	671.53	0.87	1.85	2.15	0.88	1.86	2.28
182.60	673.11	0.87	1.85	2.14	0.87	1.86	2.27
182.71	677.47	0.86	1.84	2.14	0.86	1.85	2.27
182.71	677.61	0.87	1.85	2.15	0.87	1.85	2.28
182.76	679.43	0.87	1.85	2.15	0.87	1.86	2.28
182.78	680.38	0.87	1.85	2.15	0.87	1.86	2.28
182.80	681.38	0.87	1.85	2.14	0.87	1.85	2.27
182.82	682.05	0.87	1.84	2.14	0.87	1.85	2.27
182.83	682.66	0.86	1.84	2.14	0.87	1.85	2.27
182.85	683.53	0.86	1.83	2.13	0.86	1.84	2.26
182.88	684.48	0.86	1.84	2.13	0.86	1.85	2.26
182.90	685.61	0.86	1.84	2.13	0.86	1.85	2.26

182.93	686.60	0.85	1.83	2.13	0.86	1.84	2.26
183.15	696.15	0.84	1.81	2.08	0.84	1.82	2.21
183.34	704.23	0.82	1.81	2.09	0.83	1.81	2.22
183.79	723.67	0.83	1.81	2.11	0.83	1.82	2.25
183.89	728.37	0.82	1.82	2.09	0.83	1.83	2.22
183.91	728.86	0.83	1.81	2.11	0.83	1.82	2.24
184.46	753.96	0.82	1.79	2.03	0.82	1.80	2.16
184.69	764.36	0.81	1.80	2.07	0.81	1.81	2.20
185.61	802.36	0.79	1.76	1.98	0.79	1.76	2.10
185.84	813.21	0.79	1.77	2.03	0.79	1.78	2.15
186.76	858.66	0.75	1.71	1.92	0.75	1.72	2.04
186.79	860.13	0.76	1.74	1.98	0.76	1.75	2.10
186.96	868.35	0.77	1.75	1.99	0.78	1.76	2.11
186.97	868.89	0.78	1.76	1.99	0.79	1.77	2.11
187.94	919.17	0.76	1.72	1.95	0.77	1.73	2.07
188.28	937.74	0.80	1.76	2.05	0.80	1.76	2.17
189.00	976.98	0.75	1.71	1.97	0.75	1.72	2.09
189.32	994.58	0.77	1.73	1.99	0.77	1.74	2.11
190.42	1058.16	0.70	1.67	1.91	0.71	1.68	2.02
191.50	1123.63	0.71	1.66	1.87	0.71	1.67	1.98
192.72	1201.30	0.68	1.63	1.84	0.68	1.64	1.95
194.21	1301.78	0.63	1.57	1.76	0.63	1.58	1.87
195.18	1370.35	0.60	1.55	1.72	0.60	1.55	1.82
196.29	1452.72	0.67	1.61	1.74	0.67	1.61	1.84
196.88	1497.78	0.67	1.57	1.68	0.67	1.57	1.77

197.41	1539.83	0.61	1.55	1.67	0.62	1.56	1.77
199.04	1672.98	0.57	1.51	1.61	0.57	1.51	1.70
199.86	1743.60	0.60	1.50	1.55	0.61	1.50	1.63
202.04	1941.37	0.51	1.44	1.50	0.51	1.44	1.56
202.11	1948.19	0.51	1.42	1.44	0.51	1.42	1.52
202.81	2016.17	0.54	1.43	1.41	0.54	1.43	1.49
203.57	2090.93	0.51	1.40	1.40	0.51	1.40	1.48
205.70	2313.02	0.40	1.33	1.32	0.40	1.33	1.39
206.43	2393.61	0.42	1.31	1.23	0.42	1.30	1.30
207.64	2530.23	0.39	1.27	1.19	0.39	1.27	1.25
209.51	2755.01	0.19	1.20	1.08	0.19	1.20	1.14
211.39	2994.58	0.24	1.15	1.00	0.24	1.15	1.05
212.51	3145.63	0.16	1.10	0.88	0.16	1.09	0.93
214.68	3452.45	0.08	0.98	0.77	0.09	0.98	0.81
215.80	3620.10	=0.02	0.95	0.64	=0.01	0.95	0.68
216.81	3776.26	=0.09	0.92	0.51	=0.08	0.91	0.55
218.01	3966.93	=0.12	0.89	0.51	=0.11	0.89	0.54
218.09	3980.91	=0.23	0.70	0.37	=0.22	0.70	0.39
218.50	4048.47	=0.23	0.80	0.42	=0.22	0.80	0.45
219.34	4188.07	=0.51	0.55	0.09	=0.49	0.55	0.10

a) P_N , vapor pressure of " N_2 O" sample in int. mm.Hg; for

A $10^3 \Delta P/P_N$ $^{14}N_2^{16}O$ vs $^{14}N^{15}N^{16}O$

B $10^3 \Delta P/P_N$ $^{14}N_2^{16}O$ vs $^{15}N^{14}N^{16}O$

C $10^3 \Delta P/P_N$ $^{14}N_2^{16}O$ vs $^{14}N_2^{18}O$

D $10^3 \ln(fc/fg)$ $^{14}N_2^{16}O$ vs $^{14}N^{15}N^{16}O$

E $10^3 \ln(fc/fg)$ $^{14}N_2^{16}O$ vs $^{15}N^{14}N^{16}O$

F $10^3 \ln(fc/fg)$ $^{14}N_2^{16}O$ vs $^{14}N_2^{18}O$

Table V. Triple Point Temperatures and Pressures
of the Isotopic Nitrous Oxides

Species	T_{tr} (°K)	P_{tr} (mmHg)
$^{14}\text{N}_2^{16}\text{O}$	182.25 ₉	659.03 ₇
$^{14}\text{N}_2^{18}\text{O}$	182.32 ₄	660.12 ₅
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	182.32 ₉	661.25 ₅
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	182.31 ₁	659.96 ₄

Table VI. Contributions of the translation, libration, internal vibration and non-classical rotation to the solid-vapor reduced partition function ratio of the isotopic N_2O molecules ($^{14}\text{N}_2^{18}\text{O}/^{14}\text{N}_2^{16}\text{O}$).

	$A(^{\circ}\text{K})^2$	$B(^{\circ}\text{K})$	$C(^{\circ}\text{K})^{-1}$
"Translation" ^a	96.59	0.0863	
"Libration" ^a	45.58	0.0311	-6.11×10^{-7}
Bending vibration	-0.52	0.0303	
Stretching vibration		-0.1204	
G(I, I')		-0.0113	
Total	141.65	0.0160	-6.11×10^{-7}
Experimental (least square)	141.6	0.0160	-6×10^{-7}

^a For significance of "Translation" and "Libration", see text.

Table VII. Contributions of the translation, libration, internal vibration and non-classical rotation to the solid-vapor reduced partition function ratio of the isotopic N_2O molecules ($^{15}N^{14}N^{16}O/^{14}N_2^{16}O$)

	$A(^{\circ}K)^2$	$B(^{\circ}K)$	$C(^{\circ}K)^{-1}$
"Translation" ^a	20.70	0.0185	
"Libration" ^a	82.37	0.0563	-1.10×10^{-6}
Bending vibration	-0.33	0.0224	
Stretching vibration		-0.1428	
$G(I, I')$		-0.0068	
Total	102.74	-0.0524	
Experimental (least square)	102.7	-0.0524	-1×10^{-6}

^aFor significance of "Translation" and "Libration", see text.

Table VIII. Contributions of the translation, libration, internal vibration and non-classical rotation to the solid-vapor reduced partition function ratio of the isotopic N_2O molecules ($^{14}\text{N}^{15}\text{N}^{16}\text{O}/^{14}\text{N}_2^{16}\text{O}$).

	$A(^{\circ}\text{K})^2$	$B(^{\circ}\text{K})$	$C(^{\circ}\text{K})^{-1}$
"Translation" ^a	30.92	0.0276	
"Libration" ^a	4.69	0.0032	-6.29×10^{-8}
Bending vibration	37.68	-0.1504	
Stretching vibration		0.0440	
G(I, I')		-0.0000	
Total	73.29	-0.0756	-6.29×10^{-8}
Experimental (least square)	73.3	-0.0756	

^a For significance of "Translation" and "Libration", see text.

Table IX. F Matrices of N_2O and CO_2 (in Millidynes/Å)

N_2O				CO_2			
Description	Gas	Solid-Gas	Liquid-Gas ^a	Description	Gas	Solid-Gas	Liquid-Gas
N-N stretch	18.480	+0.150	0	C-O stretch	15.483	-0.019	-0.019
N-O stretch	11.830	+0.060	0				
stretch-stretch	1.130	+0.134	0	stretch-stretch	1.287	+0.054	+0.054
N-N-O bend	0.525	+0.013	0	O-C-O bend	0.572	-0.004	-0.004
translation	0	0.160	0.134	translation	0	0.174	0.136
libration	0	0.182	0.072	libration	0	0.204	0.087
bend-lib	0	0.001	0				
bend-trans	0	-0.019	0				
trans-lib	0	-0.026	-0.026	trans-lib	0	-0.028	-0.028

a) Liquid in the neighborhood of the triple point. The values for higher temperatures are given by Eq'ns (16), (17) and (18) in the text.

Table X. Shifts in the Internal Frequencies of the Isotopic
 N_2O Molecules on Condensation ($\delta\nu = \nu_{\text{solid}} - \nu_{\text{gas}}$ in cm^{-1})

	$\delta\nu_1$ (2224)		$\delta\nu_2$ (1285)		$\delta\nu_3$ (589)	
	obs.	cal.	obs.	cal.	obs.	cal.
$^{14}\text{N}_2^{16}\text{O}$	14-35	-0.80	7.6-14.1	8.08	1.0-6.2	7.69
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	18-19	-0.68	-25~9	8.00	-	7.36
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	7-30	-1.04	8.7-12.5	8.13	-	7.74
$^{14}\text{N}_2^{18}\text{O}$	0	-0.60	(13.7-15.2)	7.71	-	7.76

Table XI. Contributions of the translation, libration, internal vibration and non-classical rotation to the liquid-vapor reduced partition function ratios of the N_2O molecules ($T = 182.26^\circ K$).

	$T^2 \ln(f_c/f_g)$		
	$\frac{{}^{14}N_2 {}^{18}O}{{}^{14}N_2 {}^{16}O}$	$\frac{{}^{15}N {}^{14}N {}^{16}O}{{}^{14}N_2 {}^{16}O}$	$\frac{{}^{15}N {}^{15}N {}^{16}O}{{}^{14}N_2 {}^{16}O}$
"Translation" ^a	22.1	58.3	27.9
"Libration" ^a	51.9	4.3	2.5
Internal vibration	-1.4	-0.7	-1.1
G(I, I')	2.1	1.2	0.0
Total	74.7	63.1	29.3
Experimental	76.1 ± 0.5	61.7 ± 0.5	29.1 ± 0.5

^a For significance of "Translation" and "Libration", see text.