

Head-tail disorder and reorientation in solid N₂O and CO: Dielectric study

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The rate of molecular reorientation in solid N₂O and α -CO is obtained from audio-frequency dielectric measurements. Both sets of data obey the Arrhenius expression. The rates extrapolate to mean reorientation times of one hour at temperatures well above the predicted dipolar ordering temperatures. Hence, the residual entropy in these solids is shown to be a kinetic effect. The size of the reorientational part of the susceptibility and the best residual entropy values show that N₂O has no short-range dipolar order while solid α -CO has a significant antiferroelectric short-range order. The mechanism of reorientation in α -CO is shown to be 180° rotations; N₂O is believed to reorient with the aid of some intrinsic defect.

INTRODUCTION

Solid N₂O and CO have been known to possess residual disorder since the calorimetric measurements of Giaque and his co-workers.^{1,2} Because the residual entropy was found to be approximately $k \ln 2$ per molecule and because the molecules of CO and N₂O (NNO) are nearly symmetric head for tail, Giaque proposed that these substances form crystals in which the molecules are randomly oriented head for tail. It was further supposed that the molecular reorientation rate ω_R becomes vanishingly small at temperatures low enough to cause head-tail (dipolar) ordering of these barely asymmetric molecules. Hence, the head-tail disorder occurring at high temperatures is kinetically frozen-in at lower temperatures.

More recent specific-heat measurements extending to 1.8 K (N₂O, Ref. 3) and 0.8 K (CO, Refs. 4 and 5) found no thermal evidence for dipolar ordering down to these temperatures. An electrostatic calculation by Melhuish and Scott compared the energies of the dipolar ordered and disordered states.⁶ Using mean-field theory, they estimated that dipolar ordering should occur near $T_C = 11$ K in N₂O and 5 K in CO. That the specific heats show no rise well below the predicted T_C is evidence that these solids have long head-tail reorientation relaxation times near and below T_C .

Because the molecules are barely asymmetric, x rays are not effective for measuring the degree of head-tail order. However, a neutron scattering experiment in N₂O at 77 K was consistent only with a structure with no long-range dipolar order.⁷

The behavior of CO bears closely on the order

and kinetics of the very similar molecules CN⁻ in the alkali cyanides. Both NaCN and KCN show three solid phases of progressively increasing CN⁻ orientational order as the temperature is reduced: a disordered phase, an elastically ordered phase where the CN⁻ are parallel or antiparallel to one crystal axis, and a dipolar ordered state believed to be antiferroelectric.^{8,9} However, RbCN never dipolar orders¹⁰; this is believed to be a kinetic effect as in N₂O and CO.

We report here dielectric measurements on solid N₂O and CO which determine the molecular reorientation rate ω_R as a function of temperature¹¹; this is possible because of the permanent electric dipole moments of N₂O and CO. The data provide clear support for the nonequilibrium view first expressed by Giaque.

EXPERIMENTAL

Ultra-high-purity N₂O and research-grade CO were purchased in cylinders from Matheson. The samples were condensed into a shielded, three-terminal capacitor cell (10 pf empty) located in a home-built, gas-flow, variable-temperature Dewar. An ac bridge operating in the audio frequency range served to measure the real and imaginary parts of the dielectric constant (ϵ' and ϵ'' , respectively). The bridge was designed around a ratio transformer and used a lock-in amplifier as the null detector. A carefully calibrated resistor network served as the resistive arm of the bridge.

Temperatures were measured with a copper-constantan thermocouple located at the top of the

6-cm-high cell. For the last N₂O run, a Pt resistance thermometer was installed and both thermometers were calibrated at room temperature, the boiling point of N₂, and the melting point of N₂O. During the last CO run, a calibrated carbon-in-glass resistance thermometer from Lake Shore was used. The reported temperatures are believed accurate to ± 0.5 K for N₂O and ± 0.25 K for CO.

RESULTS AND DISCUSSION

In solid N₂O, dielectric dispersion and loss at audio frequencies are observed from T_{melt} (see Table I) to 147 K. This is interpreted as arising from the reorientation of the permanent dipole of N₂O. The loss peak is of the Debye shape and Cole-Cole plots¹² (ϵ'' vs ϵ') of the data are semicircular with centers on the ϵ' axis. Hence, the polarization relaxation is characterized by a single time constant τ_p which is a function of temperature. The maximum of ϵ'' occurs at a frequency ω such that $\omega\tau_p = 1$. The time constant τ_r for reorientation of any individual molecule is approximately the same as τ_p .¹² Neglecting the distinction between τ_p and τ_r and defining $\omega_R \equiv \tau_R^{-1}$, one has $\omega_R = \omega$ at the maximum of ϵ'' .

The observed values of ω_R are plotted against reciprocal temperature in Fig. 1. The straight line is a fit of the data to the Arrhenius equation,

$$\omega_R = \omega_0 \exp(-E/kT). \quad (1)$$

The line corresponds to $E/k = 6020$ K and $\omega_0 = 5.6 \times 10^{19} \text{ s}^{-1}$.

All three samples of N₂O were taken from the same cylinder; the contents were at saturation and

TABLE I. Constants and values for N₂O and CO.

	N ₂ O	CO
$T_{\text{melt}}^{\text{a,b}}$	182.4 K	68.1 K
$T_{\alpha\beta}$		61.55 K
T_C^{c}	11 K	5 K
$T_{1\text{h}}^{\text{d}}$	112 K	17.5 K
μ^{e}	0.166 D	0.112 D
ϵ_0^{f}	2.193	1.809
$\epsilon_\infty^{\text{f}}$	1.984	1.5455

^aN₂O values from Ref. 3.

^bCO values from Ref. 2; CO has a high-temperature rotor phase β and a low-temperature α phase.

^cEstimated dipolar ordering temperatures from Ref. 6.

^dTemperature such that $\omega_R = 1 \text{ h}^{-1}$, extrapolated from data reported here.

^eFrom Ref. 6.

^fThe low- and high-frequency limiting values of ϵ at 162 K (N₂O) and 29.65 K (CO).

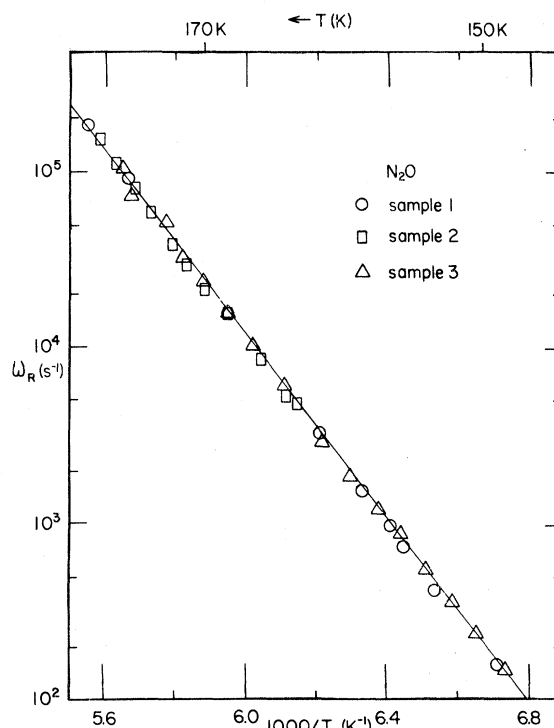


FIG. 1. Reorientation rate ω_R of N₂O in the solid. Data from three samples are shown. Line is a fit of all three sets of data using the Arrhenius equation, $\omega_R = \omega_0 \exp(-E/kT)$.

hence split in two phases. The first two samples were taken from the top of the cylinder and are expected to be rich in light, low-boiling impurities. The bottle was inverted for the third sample, so it is expected to contain heavy, high-boiling impurities. The data from all three samples agree well, so impurities evidently did not influence the data.

Dielectric loss and dispersion are observed in solid α -CO from 25 to 35 K. Using the same analysis as for N₂O, the molecular reorientation rate ω_R of CO is plotted in Fig. 2 as a function of reciprocal temperature. The offset between the two sets of data is about 0.3 K and is probably due to the copper-constantan thermocouple used for the first sample. The second set of measurements relied on a calibrated carbon-in-glass resistance thermometer and is believed to be more accurate. The straight line corresponds to an Arrhenius-equation fit to the second set of data with $E/k = 737$ K and $\omega_0 = 4.9 \times 10^{14} \text{ s}^{-1}$. The loss peaks were found to be of the Debye form with semicircular Cole-Cole plots, centered on the ϵ' axis. Hence, the relaxation of polarization in CO is exponential.

The reorientation rate data for N₂O in Fig. 1 may be extrapolated to $\omega_R = 1 \text{ h}^{-1}$ at 112 K and

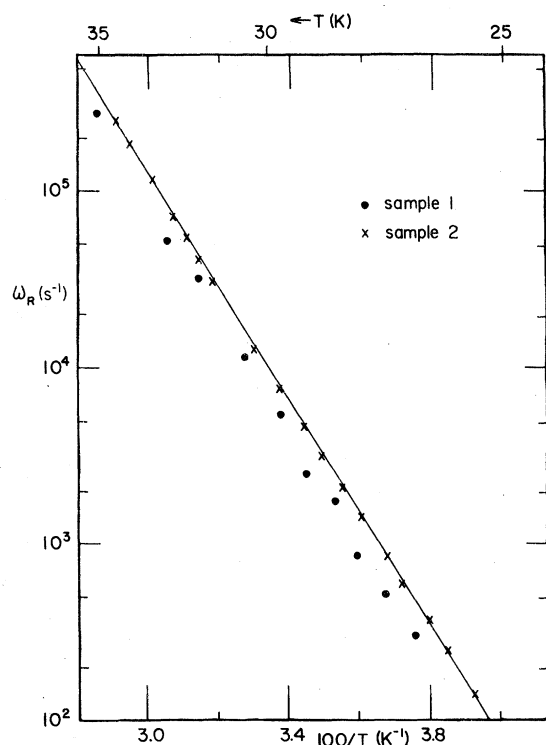


FIG. 2. Reorientation rate ω_R of CO in two different solid samples. Line is fit to the data of the second sample, where the thermometer was more accurate.

$\omega_R = (10 \text{ h})^{-1}$ at 107.5 K. Hence, molecular orientation is locked-in on laboratory time scales long before the predicted occurrence of dipolar ordering at 11 K.⁶ Similarly, extrapolation of the CO data yields $\omega_R = 1 \text{ h}^{-1}$ at 17.5 K and $\omega_R = (10 \text{ h})^{-1}$ at 16.6 K. These are much higher than the predicted T_C of 5 K.⁶ Workers at Osaka observed¹³ an anomaly in the specific heat of CO near 17 K. Thermal relaxation times of the order of a few hours at 17 K were found and ascribed to slow head-tail reorientations, in agreement with the results reported here. Hence, as Giaque originally proposed, these solids are out of thermodynamic equilibrium with respect to one set of variables: the head-tail (i.e., ± 1) orientations of the molecules.

The CO molecules in α -CO reorient by 180° rotations (head-tail flips). Nuclear quadrupole resonance (NQR) experiments in ^{17}CO find a fairly narrow line from 30 K to $T_{\alpha\beta}$.¹⁴ Rotations of the molecules by 180° will not affect the NQR line because the intramolecular electric field gradient is an axially symmetric second-rank tensor and is invariant under 180° rotations. Rotations through other angles¹⁵ would produce a very wide NQR line when ω_R is large and a strong temperature

dependence of the NQR frequency. None of these effects is observed.¹⁴ Further evidence comes from ^{13}CO nuclear magnetic resonance which finds a powder-pattern line shape due to chemical-shift anisotropy which is only weakly temperature dependent from 4 K to $T_{\alpha\beta}$.¹⁶ Rotations by 180° do not produce line narrowing because the chemical shift is also a second-rank axially symmetric tensor. Rotations by other angles would produce line narrowing, which is not observed.

The simple mechanism proposed for CO reorientation is consistent with the observed pre-exponential frequency $\omega_0 = 4.9 \times 10^{14} \text{ s}^{-1}$. This is somewhat larger than the torsional frequency of 70 cm^{-1} observed with ir (Ref. 17); we do not know if the discrepancy is real, given the large extrapolation implicit in the determination of ω_0 . The observed activation energy of 737 K may be compared to the librational-mode frequency. Assuming a simple $\sin^2\theta$ potential (which neglects the distinction between ends of the molecule, as is appropriate at $T \gg T_c$) and using the CO bond length of 1.128 \AA (Ref. 18) the librational mode at 70 cm^{-1} implies an energy barrier to head-tail flips of 934 K.¹⁷ The agreement is reasonable, given that the potential may be more complex than assumed here.

Thermal equilibrium lattice defects such as vacancies are almost certainly not involved here, because the reorientations are rapid ($\sim 10^4 \text{ s}^{-1}$) even at $T_{\alpha\beta}/2$, where these defects should be essentially absent. According to the supplier, the only impurities present in the CO in sizeable concentrations ($> 10 \text{ ppm}$) are N_2 and O_2 . These are so similar in size and boiling point to CO that they probably do not affect the data at the ~ 50 -ppm level.

The pre-exponential frequency of $5.6 \times 10^{19} \text{ s}^{-1}$ observed in N_2O is much too high to be consistent with simple head-tail flips. The reorientation rate is sizeable only near T_{melt} , which suggests that thermal equilibrium defects in the solid are involved. As remarked earlier, impurities are not involved in the N_2O reorientation. We suggest the following mechanism: In the $Pa3$ structure (an orientationally ordered form of fcc) of N_2O , all 12 nearest neighbors of any molecule are nonparallel to the central molecule.¹⁹ Hence, if any molecule executes a jump into a nearest-neighbor site that was occupied by a vacancy, it will reorient by $\theta \neq 180^\circ$ to the equilibrium orientation of its new site. Some support for this comes from the rate of translational diffusion in rare-gas solids, a monovacancy jump process. In solid Kr at the melt, the jump rate is approximately $7 \times 10^6 \text{ s}^{-1}$.²⁰ Al-

though N₂O is not a rare-gas solid, the similar value for ω_R of $2.65 \times 10^5 \text{ s}^{-1}$ at the melt suggests that vacancies may be involved in N₂O reorientation.

In general, relaxation processes that proceed by diffusion (such as spin relaxation via spin diffusion) do not lead to exactly exponential recoveries. It has been stated²¹ that observation of exponential recovery of polarization excludes mechanisms such as we have proposed: molecular reorientation (with high probability) upon the arrival of a diffusing defect. However, we have performed random-walk simulations on a computer and find the resulting recoveries indistinguishable from exponential. This is to be expected: For a single vacancy relaxing a cube of atoms ($N \times N \times N$) it takes $\sim N^3$ steps for substantial relaxation to occur. But since only N^2 steps are required for the vacancy to move across the cube, the vacancy "loses knowledge of its past location" in a time small compared to the relaxation time. Hence, for large N (small concentration of vacancies) a nearly exponential decay should result. In detail, our model was an initially fully-up-polarized system of N^3 molecules ($N=5$ and $N=10$, reasonable defect concentrations). As the vacancy landed on any site, it reoriented that site to the down direction. The vacancy was allowed to move in a random direction ($\pm X$, $\pm Y$, or $\pm Z$) every unit of time. The result, however, is believed to be independent of the model used. Interestingly, the simulations also yield exponential decays in both 15×15 and 30×30 two-dimensional arrays.

The librational frequency of N₂O in the solid is 70 cm^{-1} . This leads to an estimated barrier to simple reorientation (head-tail flips) of 4200 K^3 using the same assumptions as for CO. This barrier is smaller than the 6020-K observed activation energy attributed to a defect mechanism. It may be that the higher energy process dominates ω_R because of its very large ω_0 . In that case, at low enough temperatures the low-energy process will dominate. Assuming the 4200-K barrier value and $\omega_0 = 2.5 \times 10^{14} \text{ s}^{-1}$ for the low-energy process and the observed values for the high-energy process, the crossover occurs near $\omega_R = 10^2 \text{ s}^{-1}$ and 147 K, near where our data end. Hence, there is some reason to expect a change in slope in Fig. 1 if the data were extended to lower temperatures.

The Debye equation gives ϵ_∞ , the high-frequency limiting value of the dielectric constant as well as the low-frequency limiting value ϵ_0 :

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N}{3} \alpha$$

and

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi N}{3} \left[\alpha + \frac{\mu^2}{3kT} \right], \quad (2)$$

where N is the number density of molecules, α is their polarizability, and μ is the permanent dipole moment.²² These may be combined to yield

$$\mu^2 = \frac{9kT}{4\pi N} \left[\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right]. \quad (3)$$

Equations (2) apply not only to isotropic reorienting dipoles, but to CO and N₂O as well. Case I: Assume each dipole must be parallel or antiparallel to a fixed axis. In CO and N₂O, this axis in the $Pa3$ structure¹⁹ is one of the four body diagonals of a cube. Each axis makes an angle θ with the applied \vec{E} ; it can be shown that $\langle \cos^2 \theta \rangle = \frac{1}{3}$ regardless of the direction of \vec{E} , where the average is over the four axes. This $\frac{1}{3}$ average leads to the $\mu^2/3$ in Eq. (2). If the sample is polycrystalline, as is likely, $\langle \cos^2 \theta \rangle = \frac{1}{3}$ regardless of the crystal structure. Case II: A molecule is free to align parallel or antiparallel to any of the four body diagonals. This case results in Eq. (2) because $\langle \cos^2 \theta \rangle = \frac{1}{3}$ again.

Equation (3) may be used to compare the known dipole moments of N₂O and CO with the observed dielectric constants. For N₂O at 162 K the data (Table I) yield $\mu = 0.165 \text{ D}$. Given that the sample probably did not fill the capacitor after contracting upon freezing and cooling, this agreement with the free molecule value⁶ of 0.166 D (Table I) is better than one should expect. Use of the Onsager equation²² instead of the Debye equations gives a value for μ only 1% larger because μ is small.

Because Eq. (2) is based on the assumption of statistically independent (noninteracting) dipoles, the agreement between the known and apparent values of μ is evidence that the N₂O dipoles are independent and hence devoid of short- or long-range dipolar order at 162 K. In support of this, the maximum loss at any temperature, ϵ''_{max} varies as $1/T$ to within $\sim 6\%$ over the 20% temperature interval of the data. It appears that the sample moves inside the capacitor cell during temperature changes (also the vapor pressure is not small) preventing a more accurate determination of ϵ''_{max} . The observed residual entropy³ of $1.04(\pm 0.17)k \ln 2$ indicates complete head-tail disorder. Hence, little or no short-range head-tail order develops in N₂O before the orientations are kinetically locked-in somewhere near 112 K.

For α -CO at 29.65 K the data (Table I) and Eq.

(3) predict $\mu = 0.088$ D, a good deal smaller than the free-molecule value⁶ of 0.112 D (Table I). This difference is put into perspective by noting that μ^2 determines the difference between ϵ_0 and ϵ_∞ : The observed change in ϵ (i.e., $\epsilon_0 - \epsilon_\infty$) is only 60% of that predicted by Eq. (2). The difference in the apparent and known values of μ is not all due to partial filling of the capacitor cell: The data of two CO samples agree. Further, the value of ϵ_∞ (Table I) at 29.65 K implies a value of the polarizability α in Eq. (2) which is only 15% smaller than the known value.¹⁸

We propose that the small apparent μ is due to short-range dipolar order of the antiferroelectric kind. The residual entropy of CO (Refs. 4 and 5) is only $0.68(\pm 0.15)k \ln 2$ indicating that some short-range order occurs before the orientations become frozen (the onset of long-range order would have a specific-heat signature which is not observed). The observation of the 17-K thermal anomaly¹³ in CO indicates some ordering was arrested by kinetics at that temperature. Further, the long-range dipolar ordered state in the $Pa3$ structure has nearest neighbors (1 and 2) oriented along the body diagonals such that $\vec{\mu}_1 \cdot \vec{\mu}_2 < 0$.^{23,6} Hence, the antiferroelectric short-range order may be a precursor of the ground state. Even though the first shell of neighbors contributes 130% of the dipolar energy of the ground state, it is surprising that short-range order would exist near 30 K if T_C really is as low as 5 K.

The temperature dependence of $\epsilon_0 - \epsilon_\infty$ is predicted by Eq. (2) to be essentially Curie (T^{-1}). The maximum value of $\epsilon''(\omega)$ is just half of $\epsilon_0 - \epsilon_\infty$ for a Debye loss peak. The product $\epsilon''_{\max} T$ is plotted as a function of T in Fig. 3. Over the temperature range of the data, the product $\epsilon''_{\max} T$ is essentially constant, increasing slightly at lower

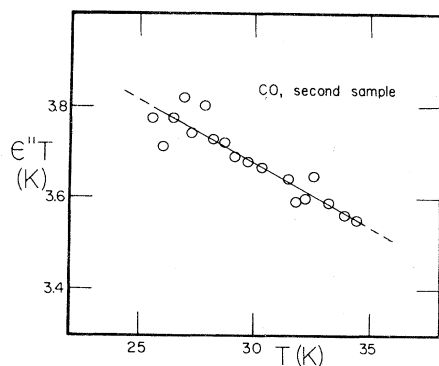


FIG. 3. Temperature dependence of $\epsilon''_{\max} T$ in α -CO. Curie behavior would result in a horizontal line.

temperatures. This is not expected in light of the antiferroelectric short-range order. It should be noted that in this temperature range the sample contraction should be small and is not expected to affect the results.

CONCLUSIONS

The rate ω_R of molecular reorientations in solid N_2O and α -CO is followed through the audio-frequency range using dielectric measurements. For N_2O , the activation energy is $E/k = 6020$ K and the preexponential frequency is $5.6 \times 10^{19} \text{ s}^{-1}$. In α -CO, the energy is 737 K and the frequency factor is $4.9 \times 10^{14} \text{ s}^{-1}$. The rates extrapolate to one reorientation per hour at temperatures 10 and 3.5 times higher than the predicted ordering temperatures in N_2O and CO, respectively. Quantum tunneling has been shown²⁴ to occur at negligible rates in α -CO; presumably this is also true in N_2O . Hence, the head-tail disorder characteristic of high temperatures is frozen into the solid before temperatures low enough to cause dipolar ordering are reached.

The size of the orientational part of the electric susceptibility is compared to the statistical prediction for noninteracting dipoles. This comparison at 162 K in N_2O indicates the dipoles are independent. Further, the residual entropy in N_2O is a full $k \ln 2$, showing that no short-range dipolar order develops before the orientations are frozen-in. In CO, however, the residual entropy is only 68% of $k \ln 2$, indicating the development of some short-range dipolar order. Further, the orientational contribution to the susceptibility in this material at 30 K is only 60% of the free-dipole value, indicating some antiferroelectric short-range order. This may be viewed as a precursor to the long-range antiferroelectrically ordered predicted ground state.

The mechanism of reorientation in α -CO involves 180° reorientations (head-tail flips). Observations of ^{17}CO NQR and ^{13}CO NMR show these molecules are always aligned parallel or antiparallel to an axis fixed in space. In N_2O , however, the large preexponential frequency for dipole reorientations is not consistent with this mechanism. Vacancies or orientational defects may be involved, although these defects do not appear to be due to impurities in the sample. NMR experiments are underway in this laboratory to determine whether reorientations in N_2O occur through 180° jumps.

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