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Dielectric anomalies of solid CO and N₂ in the audio frequency range

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Abstract

Audio frequency dielectric constant measurements of CO and N₂ in their solid phases are presented. Anomalous temperature dependence of the dielectric constant in the α -phases of both CO and N₂ and strong hysteresis effects above an onset temperature $T_h \approx 42$ K in the β -phase of pure N₂ have been observed. A simple mean-field theory is proposed which explains some of the observed anomalies in the α -phase. © 1999 Elsevier Science B.V. All rights reserved.

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Audio frequency measurements of *both* the real and imaginary components of the dielectric susceptibility of solid CO and N₂ have been carried out for the first time at temperatures ranging from their melting temperatures down to 4.2 K. These simple molecular solids have been a subject of intensive experimental and theoretical studies during the last three decades ([1–3,5,6,10,11] and the references therein). The interest in these systems derive from the fact that they serve as prototypes for studying the underlying physics of the simplest glass formers. The interactions in these solids are highly frustrated because the symmetries of the interactions and that of the lattice geometry are incompatible and as a result new phenomena occur. The molecules interact via electrostatic quadrupole moments which lead to a complex Pa3 anti-ferro-orientational ordering at low temperatures. The long range ordering is however fragile, and with the introduction of relatively small

amounts of disorder (e.g. by replacing some N₂ molecules with non interacting spherical Ar atoms) long range order is lost, and quadrupolar glass states with randomly frozen orientations are observed. These systems are believed to be analogous to the spin glasses and are particularly important because the interactions are short range and well known, and the order parameters and molecular dynamics can be studied directly.

Dielectric constant/loss measurements in these systems are particularly important because they directly probe the orientational ordering. However, only measurements at microwave frequencies have been performed in the case of solid N₂ [4]. The molecular rotations in these solids are strongly hindered, and as a consequence the relevant time scales for collective molecular reorientation are expected to be much larger than those for an ideal free rotor ($\sim 10^{-12}$ s). In fact, glassy behaviors have been

observed for solid N_2 -Ar mixtures for which the characteristic reorientational time scale is $\sim 10^{-4}$ s [2]. Measurements in this more interesting audio frequency range have not been performed due to the lack of required sensitivity. Nary et al. have carried out dielectric loss measurements of solid CO [5] in the audio frequency range, but to fully ascertain the nature of the dipolar reorientations in the geometrically frustrated β as well as the ordered α -phases, one also needs to study the dielectric constant in the entire temperature range of the solid phase. Moreover, CO has an intrinsic dipole moment; while this makes it more accessible for dielectric studies because of the large change in its dielectric loss with temperature [5,6], it also makes it more difficult to isolate the much smaller contribution from the quadrupolar interactions which are responsible for the orientational ordering. We have developed a three terminal AC capacitance bridge [7,8] with two parts per billion sensitivity for measuring the real part of the dielectric constant [9] which allows us to study the collective orientational properties of solid quadrupolar molecular systems in the relevant audio frequency range.

Figs. 1 and 2 show the real part of the dielectric constant ε of CO and N_2 as a function of temperature T , in the 0.5 kHz to 20 kHz frequency range. The sensitivity and reliability of the apparatus can be judged from the observed jumps in $\varepsilon(T)$ at the structural phase transition at $T_{\alpha\beta}$, which is 61.57 K for CO and 35.61 K for N_2 . At this temperature the low T fcc phase, the orientationally ordered Pa3 structure (or α phase), undergoes a first order transition to a high T hcp or β phase which does not support long range orientational order at any finite temperature. A second jump in $\varepsilon(T)$ occurs at the melting transition at T_m , which is at 68.13 K for CO and 63.15 K for N_2 . Note that while the figures show ε up to three decimal place accuracy, our apparatus has a much higher sensitivity, so the error bars for ε are negligible. However, as shown by the values of $T_{\alpha\beta}$ and T_m , the accuracy in the absolute value of temperature is within 0.3 K.

In addition to the expected jumps, we observed several surprising features:

(1) For $T < 25$ K, $\varepsilon(T)$ for polar CO and non-polar N_2 are similar, including the dip in $\varepsilon(T)$ near 7.5 K. This shows the absence of any dipolar order-

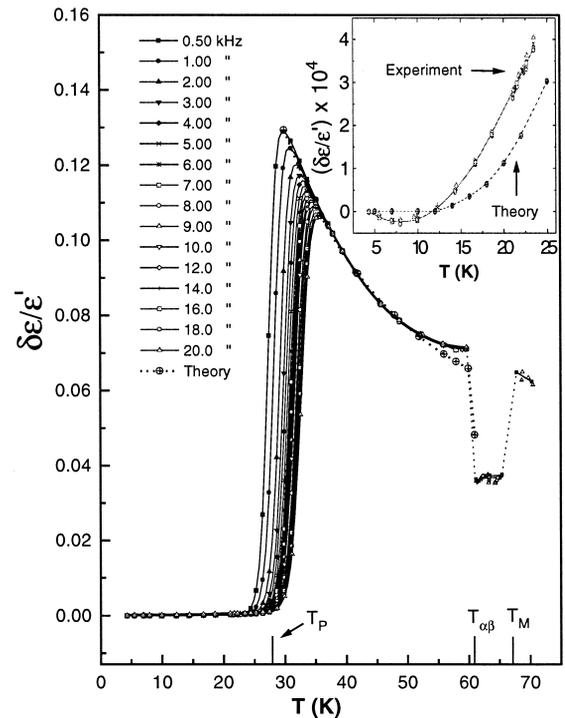


Fig. 1. Dielectric constant of pure CO in the audio frequency range relative to ε' , the value at 4.2 K. $\varepsilon' = 1.4211$ at 0.5 kHz. The inset shows the experimental and the theoretical results for the α phase below the dipolar freezing temperature T_p in greater detail.

ing in CO down to 4.2 K. Also $\varepsilon(T)$ for CO did not depend on time (of the order of several days) which would otherwise indicate a slow thermal relaxation towards a dipolar ordered state. On the other hand the dielectric response differs markedly from the conventional temperature dependence for a non-polar material described by the Clausius–Mossotti (C-M) Eq. (2) For $T > 25$ K and in the α phase, $\varepsilon(T)$ for CO is strikingly different from that of N_2 . The difference is due primarily to the dipolar contribution from CO. The sharp rise at T_p for CO can be attributed to the dipolar melting at T_p , above which dipoles begin to flip. We note that the results reported for N_2 -Ar-CO in Ref. [6] are qualitatively indistinguishable from our data for pure CO in this temperature range, except for a shift in T_p , where CO was used as a tracer to increase the dielectric response. This shows the importance of probing molecular quadrupolar systems without a dipolar tracer.

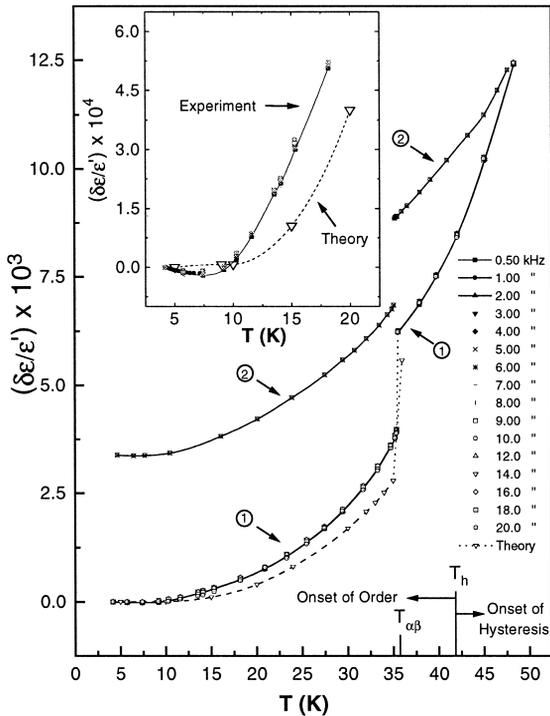


Fig. 2. Dielectric constant of pure $^{14}\text{N}_2$ in the audio frequency range relative to ε' , the value at 4.2 K on curve (1). $\varepsilon' = 1.4255$ at 0.5 kHz. Curve (2) corresponds to $\delta\varepsilon/\varepsilon'$ of the same sample heated above T_h and cooled.

(3) The most surprising feature for N_2 occurs in the β phase, where it has a highly anomalous $\varepsilon(T)$. For thermal cycling below a temperature $T_h \approx 42$ K, there is no hysteresis. In this regime, $\varepsilon(T)$ retraces a unique curve depending on the initial conditions, including the jump at $T_{\alpha\beta}$. However, if the system is taken above T_h during a heating cycle (with the AC electric field present), the observed $\varepsilon(T)$ follows a different curve during cooling, for which $\varepsilon(T)$ is higher than the previous curve. The difference between the two curves depends on how far above T_h the system was heated. Fig. 2 shows a typical hysteresis curve for a 1 kHz electric field of strength 1 kV/m where the system was heated to ~ 48 K along curve (1) and cooled along curve (2). When the system is heated to a temperature less than 48 K but above T_h and cooled, the $\varepsilon(T)$ lies between curves (1) and (2). Once the system is cooled below T_h , the corresponding $\varepsilon(T)$ curve remains reversible on thermal cycling, as long as the highest tempera-

ture remains below T_h . Within 0.1 K accuracy, $T_{\alpha\beta}$ remains the same for all curves. We should add that from these studies we cannot specify if T_h is a sharp temperature associated with the onset of hysteresis or a crossover region. We also note that the thermal resistivity data on pure N_2 [10] also has an anomaly close to T_h .

(4) If the system is left isolated (in the absence of an AC electric field) at a temperature above T_h for a long time (of the order of several hours), $\varepsilon(T)$ retraces the lowest curve, independent of the initial conditions.

(5) No hysteresis was observed for CO in the entire α phase. The small window of temperature between $T_{\alpha\beta}$ and T_m prevented us from carrying out similar measurements in the β phase of CO.

(6) The dielectric loss data for CO are similar to the results published elsewhere [5,6] but the loss data for N_2 are featureless for all frequencies and temperatures studied (not presented here).

(7) The frequency dependence of ε at low temperatures can be collapsed on a unique curve when scaled by its value at 4.2 K. This is true for curves (1) and (2) and all other intermediate curves in Fig. 2. In general at 4.2 K, ε increased with increasing frequency for both CO and N_2 ($\approx 0.06\%$ increase at 20 kHz from its value at 0.5 kHz), but we do not understand this frequency dependence. There is no frequency dependence for CO above T_p .

The existence of the strong hysteresis above T_h for pure N_2 is unexpected. The conventional picture [11] is that the β phase is an orientationally disordered phase, which becomes ordered in the α phase with a Pa3 structure. Based on our observation of the onset of hysteresis at $T_h > T_{\alpha\beta}$, we conjecture that the β phase above T_h has many available configuration states separated by small barriers in the orientational free energy. These states are responsible for the observed hysteresis. On cooling, orientational order begins to set in at T_h . At this temperature, significant configuration entropy is lost, and the system is locked in one of the available free energy minima. On cooling further, partial ordering towards a Pa3 configuration occurs, and it triggers the structural transition at $T_{\alpha\beta}$, where the α phase can in principle accommodate a complete orientational ordering. As long as the system is kept below T_h , it does not have access to the other configuration states,

and there is no hysteresis. Once the system is heated above T_h , it can access other configurations and become trapped in a different state upon cooling. The corresponding $\varepsilon(T)$ follows a different curve. Further investigation is in progress to understand if the applied AC electric field also plays a role.

While the β phase of N_2 is novel, the behavior of $\varepsilon(T)$ in the α phase is also unconventional. In order to understand the role of orientational ordering, we have developed a phenomenological model based on the known temperature dependence of the orientational order parameter for N_2 in the α phase. We find that although the molecules are large, we need to consider the discrete quantum mechanical orientational levels to explain the slow increase in $\varepsilon(T)$ in this regime. In contrast, the classical treatment gives only a linear temperature dependence. In the present model, the change in $\varepsilon(T)$ at $T_{\alpha\beta}$ to be close to the experimental value requires 50% residual orientational ordering in the β phase. This is consistent with our conjecture that the ordering begins at $T_h > T_{\alpha\beta}$. The same description holds also for CO up to the dipolar freezing temperature T_p . Above T_p the dipolar contribution overwhelms the orientational contribution. The sharp rise at T_p is associated with the onset of the flipping of the dipoles by 180° . However, the molecules are not yet free to rotate and are locked in the Pa3 structure. The subsequent decrease is therefore slower than the characteristic $1/T$ dependence expected for free dipoles. We find that a phenomenological model that accounts for the flipping without free rotation can describe the slower fall off qualitatively and predict the jump at T_p . For CO, the drop in ε at $T_{\alpha\beta}$ is consistent with the change in the order parameter with no residual ordering in the β phase. Below we briefly sketch the phenomenological model for the α phases of CO and N_2 .

The average potential energy of a diatomic molecule at a site in a crystal with Pa3 ordering can be written as

$$V = C\psi P_2(\cos\theta), \quad (1)$$

in which θ is the angle between the molecular axis and the crystal axis (\hat{Z}) at the lattice site and $P_2(\cos\theta) = -\frac{1}{2} + \frac{3}{2}\cos^2(\theta)$ [12]. The quantity ψ is the average value of $P_2(\cos\theta_j)$ for the neighboring molecules j . C (≈ -673 K for CO and ≈ -520 K

for N_2) is a function of the molecular parameters and the lattice constants [12]. The order parameter ψ is known experimentally for both CO and N_2 in the α phase but little is known about the residual ordering in the β phase. If we write $\alpha = \alpha_{\text{iso}} + \Delta\alpha$ where α_{iso} is the isotropic component and $\Delta\alpha$ is the anisotropic component of the electric polarizability of a single molecule in the condensed phase, the volume polarization can be written as [13]:

$$\mathbf{P} = \left(1 + \frac{\chi_e}{3}\right) N(\alpha_{\text{iso}} + \Delta\alpha \langle\langle \cos^2(\Omega - \theta) \rangle\rangle) \mathbf{E}_{\text{ext}}, \quad (2)$$

where χ_e is the electric susceptibility, N is the number density, Ω is the angle between the external electric field ($\hat{\mathbf{E}}_{\text{ext}}$) and $\hat{\mathbf{Z}}$, and $\langle\langle \dots \rangle\rangle$ refers to both configurational and thermal average. In the present experiment at constant volume, N is a constant. Using the known values of the order parameter ψ [11], one can calculate $\varepsilon = 1 + \chi_e$. However these calculated values of ε increase linearly with T and do not agree with our experimental results. We note that when the separation of the adjacent rotational energy levels of a rigid rotor are larger than kT , the classical Boltzmann distribution used in the averaging in (2) may not be appropriate. In fact the separation of the two lowest energy levels ($\Delta E/k$) is ≈ 93 K for N_2 and ≈ 104 K for CO (setting $\psi = 1$) [12]. From the Schrödinger equation for a rigid rotor with moment of inertia A and moving in the potential given by Eq. (1), the θ dependence is given by

$$\frac{d}{d\omega} \left[(1 - \omega^2) \frac{dQ}{d\omega} \right] + Q \left[\mu - \lambda\omega^2 - m^2(1 - \omega^2)^{-1} \right] = 0, \quad (3)$$

where $\omega = \cos\theta$, $\mu\hbar^2 = AC\psi + 2AE$, $\lambda\hbar^2 = 3AC\psi$, and E is the energy. Eq. (3) is a spheroidal wave equation and the eigensolutions $Q_{\text{lm}}(\lambda, \omega)$ are oblate spheroidal wave functions. λ is ≈ -370 K for CO and ≈ -275 K for N_2 [12]. For such large values of λ , an expansion of the eigenfunctions in terms of Laguerre polynomials is appropriate. The eigenfunctions $Q_{\text{lm}}(\lambda, \omega)$ and the eigenvalues $\mu_{\text{lm}}(\lambda, \omega)$ for several of the lowest rotational states have been calculated using the method of Flammer [14]. For various (ψ, T) sets, $\langle\langle \cos^2(\Omega - \theta) \rangle\rangle$ is calculated

first by determining Q_{lm} and μ_{lm} for several of the lowest eigenstates and the expectation values of $(\cos^2(\Omega - \theta))_{\text{lm}}$ for each of these states. Then

$$\begin{aligned} & \langle \langle \cos^2(\Omega - \theta) \rangle \rangle \\ &= \frac{1}{Z} \sum_j \gamma_j (\cos^2(\Omega - \theta))_j e^{-E_j/kT}, \end{aligned} \quad (4)$$

where Z is the partition function, γ_j is the degeneracy of the j th state and $E_j = \frac{\hbar^2}{2A} \left(\mu_j - \frac{AC\psi}{\hbar^2} \right)$. The ε calculated for N_2 using Eqs. (2,4) for various temperatures, is shown as the dashed curve in Fig. 2. This is in better qualitative agreement with the experiment. In order to obtain the correct jump at $T_{\alpha\beta}$, we need to set $\psi = 0.5$ in the β phase. The same analysis has been carried out for CO with the known order parameter, and the resulting $\varepsilon(T)$ is shown as the dashed curve in Fig. 1(inset). Again the agreement with the experiment is qualitatively better. We mention two weaknesses of the above model. First, both N_2 and CO show a small dip in $\varepsilon(T)$ near 7.5 K which remains unaccounted for in the present model. Second, if one takes the α_{iso} for a free gaseous molecule [15,16], and number density N calculated from the lattice constants [17], ε' is about 15% and 11% lower than the calculated value in the case of CO and $^{14}N_2$ respectively. In Figs. 1 and 2 we have taken ε' as the only adjustable unknown fitting parameter to compare the theory with the experiment. The lower experimental value compared to the theoretical estimate cannot be attributed to short-range antiferroelectric dipolar ordering in CO as suggested before [5] because N_2 also shows a similar behavior. However it can result from a lower polarizability of a molecule in the condensed phase than in the gaseous phase, or from a lower number density for a powdered sample than for a single crystal.

In the case of CO above T_p , the dipolar contribution to the dielectric constant should also be taken into consideration. Because the molecules are locked in the Pa3 structure, the potential in the presence of an external electric field may be written as:

$$V = C\psi P_2(\cos\theta) - \mu_o |E| f(\psi) \cos(\Omega - \theta). \quad (5)$$

The first part is the average potential energy of a single molecule as in Eq. (1). E is the internal electric field, μ_o is the intrinsic dipole moment, and f is

some function of the order parameter. Qualitatively, when ψ is unity (i.e. the molecules are completely ordered) the second term should be zero. When ψ is zero (i.e. the molecules are free to rotate) it should simply be $\mu_o \cdot E$. For simplicity, we assume f to be of the form $(1 - \psi)^r$, consistent with the above two limits. The volume polarization can be obtained for the above potential as usual. Taking the same values for the isotropic polarizability and number density which we used at 4.2 K, we find that for $f(\psi) = (1 - \psi)^{1/8}$ the experimental data can be fit very well up to $T_{\alpha\beta}$ (the dotted curve in Fig. 1). We note that the predicted change in $\varepsilon(T)$ at T_p is close to the change in the extrapolated value of the DC dielectric constant from experimental results within 0.8%. We have no explanation for the particular exponent in $(1 - \psi)^{1/8}$, but the qualitative decrease which is slower than the characteristic $1/T$ dependence of free dipoles can be understood within the model.

In summary, we have made the first measurements of the dielectric constant of pure CO and N_2 in the audio frequency range and observed several anomalous features. The low temperature behavior of both solids are very similar, but they are nevertheless very distinct from the conventional non-polar materials and can be qualitatively understood in terms of a phenomenological quantum mechanical model. The strong hysteresis effects in the β phase of pure N_2 show that the conventional picture of the onset of ordering in these frustrated systems must be modified. Because the $\varepsilon(T)$ curve always retraces the lowest curve in Fig. 2 whenever the system is left isolated at a temperature above T_h for a long time and then cooled, we strongly believe that the above hysteresis effects cannot be explained by the lattice defects such as dislocations or vacancies. However, the results are consistent with a departure from ergodicity due to trapping in a limited region of configuration space. As a consequence of the frustration of the interactions, the configuration space has a rugged landscape with many quasi-equal low energy minima separated by potential energy barriers. This phenomenon is common to a wide class of glass formers and other frustrated systems with the introduction of disorder. The most significant result of this study is that the glassy effects are produced in a purely geometrically frustrated system without the introduction of disorder. This will be relevant to

understanding the co-operative behavior in other geometrically frustrated systems (pyrochlores, spinels, and nuclear antiferromagnets).

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