Dielectric study of orientational disorder in $(CO_2)_{1-x}(N_2O)_x$ mixed crystals

R. Böhmer* and A. Loidl

Institut für Physik der Johannes-Gutenberg-Universität, D-6500 Mainz, Federal Republic of Germany

The dipolar relaxation dynamics of solid solutions of carbon dioxide and nitrous oxide has been investigated using dielectric spectroscopy. The temperature dependence of the relaxation rate reveals an ideal Arrhenius behavior for all concentrations, with energy barriers which scale linearly between the two pure compounds. The attempt frequencies are anomalously high. The distribution of relaxation times due to the static random fields as introduced by the substitutional impurity molecules is almost negligible. The melting temperature is determined by a critical relaxation rate of 40 kHz.

INTRODUCTION

Since the early x-ray investigation by Vegard,[1] it is known that nitrous oxide and carbon dioxide form solid solutions at any concentration x. The full miscibility is due to the fact that these linear molecules are isoelectronic and that both pure compounds exhibit similar structural properties: CO_2 (Ref. 2) and N_2O (Ref. 3) crystallize in a face-centered-cubic ($Pa3$) structure. This structure consists of four sublattices, on each of which the molecules are oriented along one of the four body diagonals. However, the symmetric OCO molecule is orientationally ordered,[4] whereas the nonsymmetric NNO molecule remains disordered with respect to head and tail. The existence of residual entropy at low temperatures has been demonstrated in a number of specific-heat experiments.[5] The dipolar disorder is frozen in due to high hindering barriers against reorientations and a low "hypothetic" Curie temperature ($T_C = 11$ K, Ref. 6) where electric order would be established. Thus, at the virtual ordering temperature the reorientation rates are vanishingly small and long-range electric order cannot be established on the time scale of a laboratory experiment.

A dielectric study of solid N_2O has been performed by Nary et al.[7] An Arrhenius type of behavior with hindering barriers $E/k_B = 6020$ K and an extraordinarily high attempt frequency of $2\pi\nu_0 = 5.6 \times 10^{19}$ s^{-1} have been detected. The reorientational dynamics in solid CO_2 have been studied using ^{13}C NMR (nuclear magnetic resonance). The thermally activated processes were described by a hindering barrier $E/k_B = 6600$ K and an attempt frequency of $2\pi\nu_0 = 2 \times 10^{17}$ s^{-1}. The Arrhenius-type relaxation was interpreted as coupled rotational-translational jumps owing to the equal rates of reorientation and translation which have been measured in separate NMR experiments.[8] Solid solutions of CO_2 and N_2O have been investigated utilizing infrared[9] and Raman[10] techniques. In the Raman study a one-mode behavior, characterized by a linear shift of the frequency of the librational mode, was observed.[10]

At present we are interested in the relaxation dynamics of molecular crystals with respect to competing interactions such as multipolar forces, lattice anisotropies, and random strains, which are introduced by the substitutional impurities. In orientational glasses[11] the reorienting moments undergo a cooperative freezing process devoid of long-range multipolar order. In these systems the interaction forces are usually stronger than the lattice anisotropy. $(CO_2)_{1-x}(N_2O)_x$ is a system dominated by the lattice anisotropies, i.e., the hindering barriers are high and the dipolar interaction forces are relatively weak. Here we expect that any distribution of relaxation times must be due to random strains. In the following, we present the results of our studies of N_2O dipoles in a carbon-dioxide host and of pure nitrous oxide. We determine the energy barriers and attempt frequencies and compare these results with the NMR data of Ref. 8 which have been determined in pure CO_2. Finally we discuss our results with those obtained in similar solid solutions such as $(N_2)_{1-x}(CO)_x$ and $(Ar)_{1-x-y}(N_2)_y(CO)_x$.

EXPERIMENTAL DETAILS AND RESULTS

Due to the high triple-point pressure of carbon dioxide (99.995% nominal purity) the condensation of liquids containing CO_2 required operation with relatively high pressures. Pure nitrous oxide (nominal purity 99.8%) was condensed through a heated capillary into a dielectric cell as described previously.[12] To grow crystals of a given concentration, the gas mixtures were condensed from the storage vessel onto the walls of the cold capillary ($T \approx 30$ K). Then the empty storage volume was closed and the capillary heated to room temperature. Heating additionally the sample holder gave pressures up to 6 bars, which caused the binary mixtures to liquify. Then the solutions were allowed to homogenize for at least 1 h. Finally, they were solidified and cooled slowly to the temperatures of liquid helium. The mixed crystals with concentrations $x = 0.26$ and 0.5 were grown by the admixture of CO_2 to crystals already present in the cell: i.e., a defined amount of CO_2 gas was condensed into the loaded measuring cell and capillary and then the same procedure as outlined above was followed. Thus the un-

certainty in the composition of these mixed crystals was relatively large (see Fig. 5). For $(CO_2)_{0.96}(N_2O)_{0.04}$ the chemicals were mixed as gases and condensed into the measuring cell according to the freeze-thaw procedure described above.

All measurements of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$ were performed using a Hewlett-Packard HP-4274 LCR meter which operates in the audiofrequency range ($10^2 - 10^5$ Hz). In the liquid state the real part of the permittivity ϵ' of each sample varied linearly with temperature. On cooling into the solid phase, a marked discontinuity occurred which was taken as the signature of crystallization. Below the melting point, dielectric dispersion was observable in the audiofrequency regime over a range of approximately 40 K.

The results for pure N_2O are in agreement with the data published by Nary et al.[7] Solid solutions have been studied for $x = 0.04$, 0.26, and 0.5. As an example, Fig. 1 shows the complex dielectric constant of $(CO_2)_{0.5}(N_2O)_{0.5}$ versus temperature for different measuring frequencies. Clear dispersion effects are visible just below the melting point of the binary liquid. The dispersion effects were shifted to lower temperatures for higher N_2O concentrations x. The height of the loss peaks scaled almost linear with x. Figure 2 shows the dielectric loss $\epsilon''(T)$ in $(CO_2)_{1-x}(N_2O)_x$ for concentrations $x = 0.26$, 0.5, and 1. The measuring frequency was 1 kHz. It is readily seen that ϵ'' reveals almost ideal Debye behavior for all concentrations.

Finally, Fig. 3 shows a Cole-Cole representation of the complex dielectric constant in solid solutions of CO_2 and N_2O. Here the real part of the dielectric constant was plotted versus the dielectric loss for dipole concentrations $x = 1$ and 0.5 and at temperatures $T = 174.1$ and 183.9 K, respectively. Figure 3 reveals ideal Debye behavior for $x = 1$ and slight deviations for $x = 0.5$, possibly arising from the disturbance of the local hindering barriers due to the site disorder. Furthermore, it provides evi-

FIG. 2. Dielectric loss of three $(CO_2)_{1-x}(N_2O)_x$ crystals with $x = 0.26$, 0.5, and 1 for a measuring frequency $f = 1$ kHz. Solid lines are calculated with the Debye formula [Eq. (2)].

dence that the static dipolar susceptibility, which is determined by the diameter of the circular arc, scales almost linearly with concentration.

ANALYSIS AND DISCUSSION

In this section the temperature dependence of the relaxation times and its distribution are analyzed.

Relaxation times and energy barriers

The reorientational motion of both pure CO_2 (Ref. 8) and N_2O (Ref. 7) was previously found to obey Arrhenius laws. This implies thermally activated molecular crossing of hindering barriers E leading to a relaxation time

$$\tau = \tau_0 \exp(E/k_B T) .$$ (1)

To determine the activation energies of the mixed crystals, the temperatures of the dielectric loss maxima at a given frequency were plotted into an Arrhenius diagram. The results are shown in Fig. 4. The dipolar relaxation for all x reveals ideal Arrhenius behavior. From the slopes of the lines the values of the energy barriers were calculated. The preexponential factor τ_0 is determined by

FIG. 1. Real part of the dielectric constant of condensed $(CO_2)_{0.5}(N_2O)_{0.5}$ for different measuring frequencies.
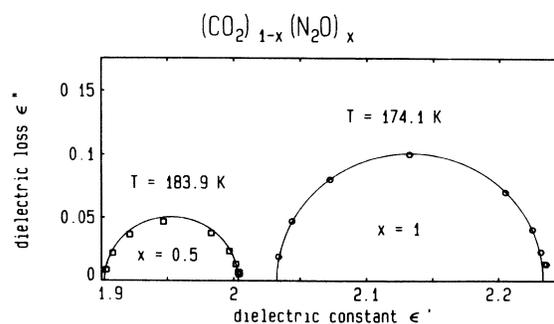
FIG. 3. Cole-Cole plot for the complex dielectric constant for $(CO_2)_{1-x}(N_2O)_x$ for concentrations $x = 1$ ($T = 174.1$ K) and $x = 0.5$ ($T = 183.9$ K).
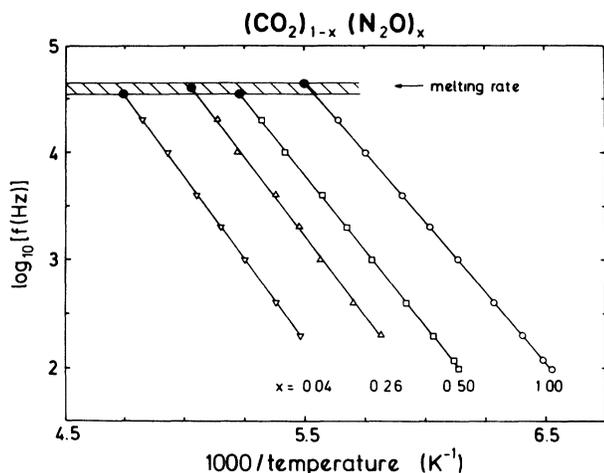
FIG. 4. Activation plot for $(CO_2)_{1-x}(N_2O)_x$ as determined from the dielectric loss maxima (open symbols). The solid lines were calculated using the energy barriers given in Fig. 5. The crosses denote melting rates. The hatched bar is drawn to guide the eye.

the value of the relaxation time at "infinite" temperatures and was found to be 10^{-20} s, almost independent of concentration with deviations from the average value of less than a factor of 10. The concentration dependence of the energy barriers is shown in Fig. 5. The values of the hindering barriers scale linearly between those of the
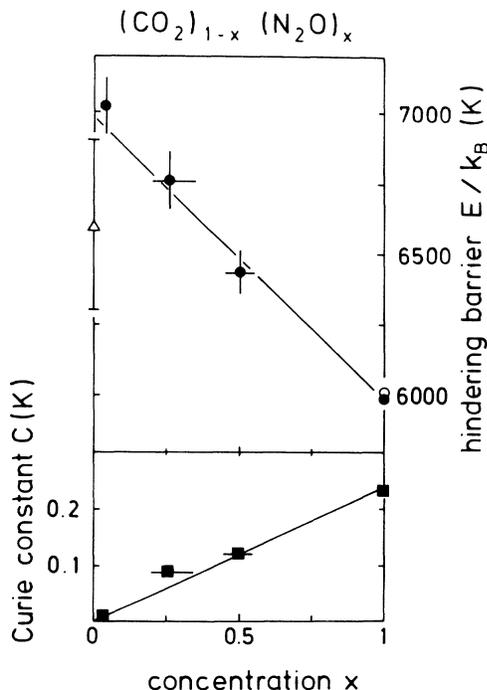
FIG. 5. Curie constants and activation energies of $(CO_2)_{1-x}(N_2O)_x$ from the present study. The energy barriers of the pure crystals were also determined by dielectric measurements ($\bigcirc$, Ref. 7) and by NMR experiments ($\triangle$, Ref. 8). Horizontal bars indicate the uncertainties in the determination of the concentration of the mixed crystals. Lines are drawn to guide the eye.

pure compounds: $x = 0$ (CO_2); $E/k_B \approx 7000$ K and $x = 1$ (N_2O); $E/k_B \approx 6000$ K. The results for the energy barriers are similar to the observations in $(N_2)_{1-x}(CO)_x$, where the barriers of the alloys interpolate between those of N_2 ($E_{N_2} = 422$ K) and CO ($E_{CO} = 737$ K).[13] Surprisingly, the barriers of all these compounds (N_2, Co, CO_2, and N_2O) are in excellent agreement with theoretical calculations of the molecular-field constant of the intermolecular interaction.[14]

The values of the attempt frequencies and hindering barriers for pure N_2O are close to the values reported from Nary et al.[7] However, the attempt frequencies of N_2O defects in CO_2 determined by the present dielectric experiments differ by a factor of 50 from the values observed in CO_2 using ^{13}C NMR techniques. The reason for this discrepancy is unclear; it might indicate that the relaxation mechanism for CO_2 in CO_2 are different from those of N_2O in CO_2. The unphysically high prefactors could be explained if one takes an entropy term, in addition to the true energy of activation, into account: e.g., a linear temperature dependence of the hindering barriers which extrapolates to $E(0$ K$) \approx 6000$ K could yield attempt frequencies in the THz range.

It is interesting to note that the energy barriers of the ternary quadrupolar glasses $(Ar)_{1-x-y}(N_2)_y(CO)_x$ determined in dielectric experiments[15] can be reproduced using $E = c$ $(xE_{CO} + yE_{N_2})$ and $c = 0.6 \pm 0.07$. This formula implies that the contributions to the local barriers due to the substitutional Ar impurities are negligible. The constant c indicates that the barriers in the glassy state are significantly lower than in the orientationally ordered state.

Figure 4 reveals another remarkable feature of $(CO_2)_{1-x}(N_2O)_x$: at a given reorientation rate these molecular compounds melt ($v_{melt} = 40$ kHz). Similar critical relaxation rates have been reported for the pure and mixed alkali cyanide crystals[16] ($v_c = 3.2$ GHz) and can be deduced from the published dielectric data[13] in $(N_2)_{1-x}(CO)_x$: $v_c = 0.25$ GHz. In these latter systems, however, the critical relaxation rate indicates the transition from an orientationally ordered state into a high-temperature plastic phase. We believe that in the solid solutions of carbon dioxide and nitrous oxide the critical relaxation rates correspond to critical mean-square displacements of translational excitations and thus can be viewed as a Lindemann type of criterion for the rotational degrees of freedom.

Using the experimentally observed librational band for N_2O at 70 cm^{-1} (Ref. 9) and assuming a $\sin^2\theta$, Nary et al.[7] estimated a hindering barrier for pure reorientational flips of 4200 K, which is significantly lower than the experimentally observed value of 6000 K. This discrepancy was interpreted by these authors in terms of combined rotational-translational jumps. It was suggested that deviations from a single activated process should become apparent in the Arrhenius plot of N_2O for frequencies near 10^{-2} Hz.[7] Due to the higher-energy barrier of CO_2, where an absorption band is in fact observable at 68 cm^{-1},[17] the proposed effect would shift to frequencies at around 1 kHz. However, no signs of anoma-

lous behavior are seen in the Arrhenius plot of $(CO_2)_{0.96}(N_2O)_{0.04}$.

Distribution of energy barriers

In order to describe the full dielectric loss spectra, a Debye model was used and the solid lines in Fig. 2 were calculated according to

$$\epsilon = \frac{C}{T} \int_0^\infty \frac{P(E')\omega\tau(E')}{1+[\omega\tau(E')]^2} dE' , \qquad (2)$$

where $P(E')=\delta(E-E')$ is a δ distribution. Using the Arrhenius parameters given above, good agreement with the experimental results was achieved (Fig. 2). As shown in Fig. 5, the Curie constants were found to scale with the dipole concentration as expected for mixed crystals. The use of the Curie law in Eq. (2) is based on the assumption that the reorientational motion of the dipoles is uncorrelated and thus only governed by local potentials.

In the mixed crystals, the local fields at N_2O sites will vary according to the statistical composition of the molecular environment. If only nearest-neighbor interactions are considered, then the distribution of fields or energy barriers will in general be given by a binomial distribution. For $x = 0.5$ this function is well approached by a Gaussian distribution. $P(E)=(\sigma\sqrt{2\pi})^{-1}\exp[-(E'-E)/(s\sigma^2)]$. For K-fold coordinated lattices the width $\sigma = \Delta E/(2\sqrt{K})$ is determined by the difference ΔE of the activation energies of the pure compounds. In the mixed crystals under consideration $\sigma = (1000 \text{ K})/(2\sqrt{12}) \approx 144$ K.

To check the relevance of this approach, we calculated the $\epsilon''(T)$ spectra for $(CO_2)_{0.5}(N_2O)_{0.5}$ using a Gaussian distribution of energy barriers. The agreement between experimental data and theoretical curves was always acceptable as long as σ was smaller than 120 K, without preference for a definite width. We conclude that our results do not contradict the results of the theoretical estimate, but they do not allow us to get clear evidence on the influence of random strains on the distribution of relaxation times.

At first glance the Cole-Cole plot for $(N_2)_{0.5}(CO)_{0.5}$ reported for a single temperature ($T=23.4$ K) by Liu and Conradi[13] suggest a rather broad distribution of relaxa-

tion times. However, the distribution estimated from their data leads to a distribution of relaxation times with a full width at half maximum of less than two decades. Thus these binary mixtures of isoelectronic molecules which are dominated by quadrupolar (elastic dipolar) interaction forces reveal a narrow distribution of energy barriers. Glassy low-temperature states, on the other hand, are characterized by a broad distribution of relaxation times corresponding to a broad distribution of local barriers against reorientations. The substitution of Ar in the N_2/CO system immediately increases the distribution width [15] and was taken as evidence for the appearance of a glassy state in these ternary solutions. Results from magnetic resonance,[18] specific heat,[19] and thermal conductivity[20] support this interpretation.

CONCLUSIONS

Dielectric spectroscopy in the audiofrequency range has been applied to solid solutions of isoelectronic CO_2 and N_2O, where the latter molecule carries a dipole moment of the order 0.17 D.[7] For all concentrations investigated the dipolar relaxation follows closely a pure Debye behavior which is characterized by a single relaxation time. From an analysis of the dielectric loss we concluded that any distribution of energy barriers in these systems must be less than approximately 120 K, which is almost in accordance with simple theoretical considerations which predict a distribution of energy barriers in the order of 140 K for $x = 0.5$.

The temperature dependence of the relaxation time follows an ideal Arrhenius behavior for all x. The observed hindering barriers scale linearly with concentration; the attempt frequencies are almost constant and anomalously high. Finally it is remarkable that at the melting transition all solid solutions are governed by a unique critical relaxation rate of $\nu_{crit} = 40$ kHz.

*Present address: Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604.

[1]L. Vegard, Naturwissenschaften 21, 443 (1931); Z. Phys. 71, 465 (1931).

[2]R. D. Etters and B. Kuchta, J. Chem. Phys. 90, 4537 (1989); W. H. Keesom and J. W. L. Köhler, Physica 1, 167 (1934).

[3]W. C. Hamilton and M. Petrie, J. Phys. Chem. 65, 1453 (1961); S. I. Kovalenko, E. I. Indan, A. A. Khudotyoplaya, and I. N. Krupskii, Phys. Status Solidi A 20, 629 (1973).

[4]W. F. Giauque and C. J. Egan, J. Chem. Phys. 5, 45 (1937); V. G. Manzhelii, A. M. Tolkachev, M. I. Bagatskii, and E. I. Voitovich, Phys. Status Solidi B 44, 29 (1971).

[5]K. Clusius, Z. Elektrochem. 40, 98 (1934); R. W. Blue and W. F. Giauque, J. Am. Chem. Soc. 57, 991 (1935); A. Eucken and H. Veith, Z. Phys. Chem. B 35, 463 (1937); T. Atake and H.

Chihara, Bull. Chem. Soc. Jpn. 47, 2126 (1974); see also A. M. Tolkachev, V. G. Manzhelli, V. P. Azarenkov, A. Ezhovski, and E. A. Kosobutskaya, Fiz. Nizk. Temp. 6, 1533 (1980) [Sov. J. Low-Temp. Phys. 6, 747 (1980)].

[6]M. W. Melhuish and R. L. Scott, J. Phys. Chem. 68, 2301 (1964).

[7]K. R. Nary, P. L. Kuhns, and M. S. Conradi, Phys. Rev. B 26, 3370 (1982).

[8]S.-B. Liu, M. A. Doverspike, and M. S. Conradi, J. Chem. Phys. 81, 6064 (1984).

[9]K. R. Witters and J. E. Cahill, J. Chem. Phys. 67, 2405 (1977).

[10]H. Yamada and W. B. Person, J. Chem. Phys. 41, 2478 (1964).

[11]A. Loidl, Annu. Rev. Phys. Chem. 40, 29 (1989).

[12]R. Böhmer and A. Loidl, J. Chem. Phys. 89, 4981 (1988); R. Böhmer, ibid. 91, 3111 (1989).

[13]S.-B. Liu and M. S. Conradi, J. Chem. Phys. **78**, 6901 (1983).

[14]V. A. Slusarev, Yu. A. Freiman, I. N. Krupskii, and I. A. Burakhovich, Phys. Status Solidi B **54**, 745 (1972).

[15]S.-B. Liu and M. S. Conradi, Solid State Commun. **49**, 177 (1984).

[16]F. Lüty and J. Ortiz-Lopez. Phys. Rev. Lett. **50**, 1289 (1983).

[17]A. Anderson and S. H. Walmsley, Mol. Phys. **7**, 583 (1964).

[18]J. H. Walton, M.-C. Wu, and M. S. Conradi, Can. J. Chem. **66**, 680 (1988).

[19]C. I. Nicholls, L. N. Yadon, D. G. Haase, and M. S. Conradi, Phys. Rev. Lett. **59**, 1317 91987).

[20]L. N. Yadon, C. I. Nichols, and D. G. Haase, Phys. Rev. B **40**, 5215 (1989).