# Heterogeneous $NO_3^-$ Ion Dynamics near the Glass Transition in the Fragile Ionic Glass Former $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$: A $^{15}N$ NMR Study

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The tumbling dynamics of the $NO_3^-$ anions in $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ liquid have been studied close to its glass transition ($T_g = 333$ K) by $^{15}N$ wide line NMR spectroscopy. The time scale of this tumbling dynamics closely corresponds to that associated with the shear or $\alpha$ relaxation in this material over 5 orders of magnitude. Clear evidence of bimodal spatial heterogeneity in this dynamics was observed close to $T_g$ within a small temperature range (340 to 365 K) with the coexistence of a slow- and a fast-tumbling population of $NO_3^-$ anions. The relevance of the existing models of cooperative dynamics near glass transition in explaining these observations are discussed. [S0031-9007(97)03057-3]

The dynamics of various relaxation processes and their relation to the nature of glass transition have been studied extensively in recent years, both from theoretical and experimental standpoints [1–8]. It has been proposed that the nature of the relaxation processes can be fundamentally different between ionic and molecular glass formers as well as between strong and fragile liquids [8]. Formation of spatiotemporal dynamical heterogeneities in supercooled glass-forming liquids has been implicitly or explicitly hypothesized to play a major role in viscous slowdown and glass transition [2,9–12]. Experimental observation of these heterogeneities and the determination of their physico-chemical nature would thus play a central role in our current theoretical understanding of the problem of glass transition [12].

In this article we report the first observation of the tumbling dynamics of $NO_3^-$ planar triangular ions in an extremely fragile liquid, $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN) by variable temperature $^{15}N$ static nuclear magnetic resonance (NMR) spectroscopy close to its glass transition ($T_g = 333$ K [13]). The CKN glass was made from 99% $^{15}N$-enriched $KNO_3$ and $Ca(NO_3)_2$ by the usual procedures [13]. The glass samples were crushed and remelted in vacuum at 533 K and sealed in pyrex tubes, followed by quenching in air in order to ensure dryness. Static $^{15}N$ spectra were obtained from 233 to 432 K with a modified Varian horizontal solenoid probe and a modified Varian VXR-400S spectrometer operating at a NMR frequency of 40.544 MHz for $^{15}N$. The temperature gradient across the sample was found to be within $\pm 1$ K. The $^{15}N$ magic angle spinning (MAS) spectrum was acquired at room temperature with a Varian MAS probe.

The static $^{15}N$ spectrum of the CKN glass at $T = 233$ K [Fig. 1(a)] is typical of a uniaxial powder pattern. With increasing temperature this line shape remains unchanged up to $T = 340$ K, a few degrees above $T_g$ (Fig. 2). The $D_{3h}$ symmetry of the $NO_3^-$ ion gives rise to such a uniaxial chemical shift anisotropy (CSA) tensor with the unique axis along the $C_3$ axis of the molecule. The CSA tensor would remain unchanged if the ion is jumping or rotating

around this axis. A number of studies using Raman scattering, the optical Kerr effect, and molecular dynamics simulation have proposed that the $NO_3^-$ ion undergoes rapid rotation on the picosecond time scale around the $C_2$ axes, even below $T_g$ [14–16]. In the case of such rapid rotation the CSA of the $NO_3^-$ ion would decrease by 50% and change its sign, although it will still remain uniaxial. However, the CSA for CKN glass ($\approx 235$ ppm) is very similar to those reported for various crystalline alkali and alkaline earth nitrates (205 to 231 ppm) for which single crystal measurements show that the orientation of the principal axis of the CSA tensor is coincident with the $C_3$ axis of the $NO_3^-$ ion [17,18]. Thus, the fast rotational dynamics of the nitrate ions in the CKN glass, as observed by Raman scattering and optical Kerr effect, has to be of a
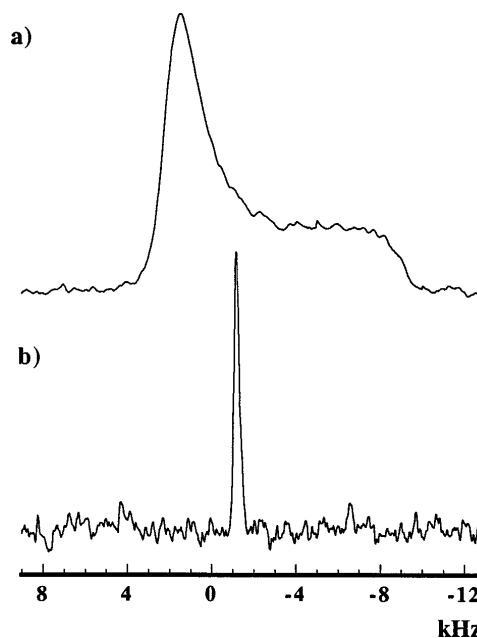


FIG. 1. (a) The $^{15}N$ static powder spectrum of CKN glass at $T = 233$ K. (b) MAS powder spectrum of CKN glass at room temperature; spinning speed equals 5.5 kHz.
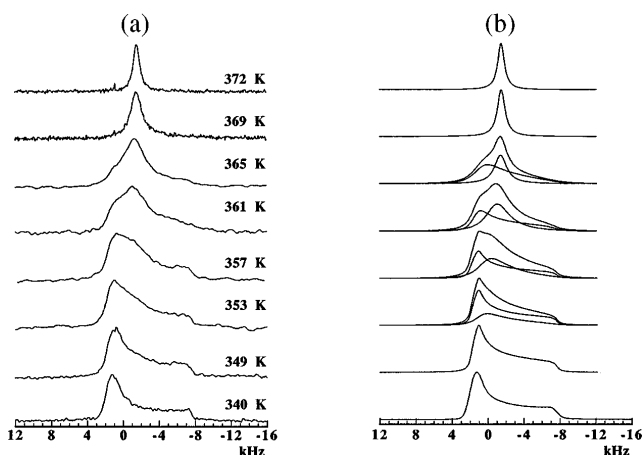
FIG. 2. (a) The experimental $^{15}N$ static NMR spectra of CKN glass and liquid at temperatures indicated, showing effects of motional narrowing on the line shape. (b) Simulated spectra at the same temperatures. For details of the simulation see text.

different nature than that postulated. The MAS spectrum [Fig. 1(b)] indicates the presence of only one type of nitrogen site in the glass within experimental resolution, with an isotropic chemical shift of $-4.6 \pm 0.5$ ppm with respect to crystalline $KNO_3$.

With an increase in temperature ($T > 340$ K), the line shape starts changing rapidly until it finally collapses to a single narrow Lorentzian peak at the isotropic chemical shift at $T \geq 367$ K, indicating rapid tumbling motion of the $NO_3^-$ ions (Fig. 2). The linewidth continues to decrease and reaches a limiting value of 24 Hz within instrumental resolution at $T \geq 395$ K. The spectral line shapes have been simulated up to $T = 372$ K, using a model of a reorientational exchange of $NO_3^-$ ions among $N$ different sites or orientations by isotropic tumbling. The analytic expression for the resulting line shape is given by the real part of $g(\omega)$ [19], where

$$g(\omega) = \frac{1}{N} \frac{L}{1 - (L/\tau_{NMR})}$$

and $L = \sum_{j=1,N}[i(\omega - \omega_j) + 1/T_{2j} + N/\tau_{NMR}]^{-1}$, $\omega_j$ is the frequency and $T_{2j}$ is the reciprocal of the intrinsic linewidth corresponding to the orientation $j$ of the ion, and $1/\tau_{NMR}$ is the frequency of the orientational exchange or the tumbling frequency of the $NO_3^-$ ions. In this analysis, the frequencies $\omega_j$ corresponding to 400 orientations ($N$) were generated by taking that many angular steps through the expression for the uniaxial powder pattern [19]. The value of $T_{2j}$ has been kept constant as 0.7 ms for all orientations in all of the simulations.

The $\tau_{NMR}$ values at $T \geq 372$ K (up to $T = 380$ K) have been obtained from the linewidths under the fast-exchange approximation [20], according to which

$$\frac{1}{T_2'} = \frac{1}{T_2} + \tau_{NMR} \sum_{i=1}^{n} P_i \delta_i^2,$$

where $T_2'$ is the measured spin-spin relaxation time at each temperature and $T_2$ is its value in the absence of exchange. $P_i$ and $\delta_i$ denote the intensities and chemical shifts, respectively, of a series of $n$ equally spaced lines under the $^{15}N$ spectral line shape in the absence of exchange. $T_2'$ and $T_2$ have been approximated as $(\pi \Delta \nu_e)^{-1}$ and $(\pi \Delta \nu_n)^{-1}$, respectively, where $\Delta \nu_e$ is the experimental linewidth at the corresponding temperature and $\Delta \nu_n$ is its limiting value determined as the limiting instrumental linewidth of 24 Hz.

A comparison of the simulated line shapes with the experimental spectra is shown in Fig. 2. For $T > 365$ K the spectra can be well simulated with a single temperature dependent tumbling frequency $(\tau_{NMR})^{-1}$. However, for temperatures $340 < T \leq 365$ K, the $^{15}N$ spectra (Fig. 2) clearly indicate that, in the case of isotropic tumbling of the $NO_3^-$ ions, the line shapes cannot be simulated with a single $\tau_{NMR}$ value. Simulations on the basis of restricted rotational jumps of the $NO_3^-$ ion about its different symmetry axes [19] also failed to reproduce such line shapes. $^{15}N$ spectra were obtained in this temperature range as a function of increasing waiting time after saturation of the magnetization, an example of which at $T = 361$ K is shown in Fig. 3. These results unambiguously show the presence of at least two dynamically distinct population of $NO_3^-$ ions with different NMR spin-lattice relaxation times ($T_1$'s). The slow tumbling population was found to have a longer $T_1$ than the fast tumbling population. The spectral line shapes in this temperature range can indeed be reasonably well simulated with a slow- and a fast-reorienting population (Fig. 2). The fraction of the slow population is found to decrease with increasing temperature, and its tumbling frequency is about an order of
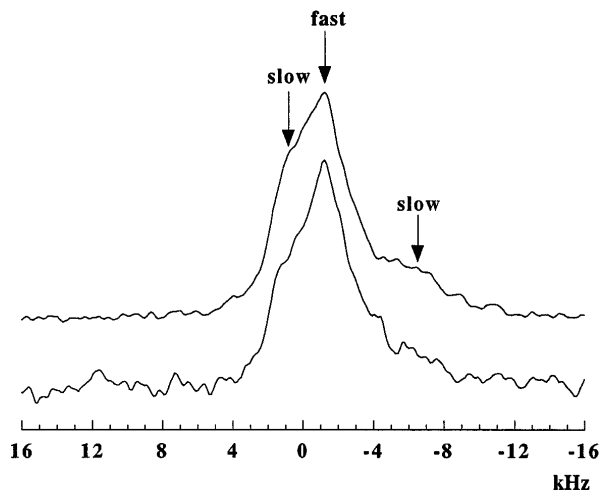


FIG. 3. The experimental $^{15}N$ static NMR spectra of CKN obtained at $T = 361$ K as a function of variable waiting times after complete saturation of the magnetization. The top and bottom spectra correspond to waiting times of 500 and 10 s, respectively. The slow- and fast-relaxing components are as shown.

magnitude smaller than that for the fast population (Table I). The simulated $^{15}$N spectral line shapes have been found to be relatively insensitive to the changes in $(\tau_{NMR})^{-1}$ in the range of a few Hz to a few hundred Hz. This is a plausible explanation for the lack of a clear two-component structure in the spectrum of CKN at $T = 349$ K. It is also consistent with the fact that the $^{15}$N spectra do not show any sign of reorientational exchange at temperatures very close to $T_g$ $(333 < T < 340$ K). We were only able to simulate the spectrum at $T = 349$ K with an average $(\tau_{NMR})^{-1}$ of $\approx 700$ Hz (Fig. 2). Two-dimensional NMR experiments are more sensitive to slow dynamics and will be able to resolve these issues in the future. The time scale of the tumbling process $\tau_{NMR}$ of individual $NO_3^-$ ions as measured in this paper (Table I) ranges between $10^{-2.84}$ and $10^{-7.91}$ s. The strong correspondence of $\tau_{NMR}$ (or its fast component, where the dynamics is heterogeneous) with the average shear relaxation time scale $\tau_{shear}$ [13], over the entire temperature range, strongly suggests that the tumbling of the $NO_3^-$ ions is closely related to the $\alpha$ process and, hence, to the glass transition in CKN (Fig. 4). The $\tau_{NMR}$ of the slow $NO_3^-$ ion population is approximately an order of magnitude longer than $\tau_{shear}$.

Temporal and/or spatial heterogeneities within the dynamics of the $\alpha$ and $\beta$ processes have previously been observed in the case of polymeric and molecular liquids close to the glass transition [5,7]. In all these cases, spatial heterogeneities were found to persist in the liquids with lifetimes much longer than the average relaxation time of the corresponding $\alpha$ or $\beta$ processes. Direct observation of spatial heterogeneity in the $NO_3^-$ tumbling dynamics is not possible with the present technique. However, the strong bimodal nature of the dynamics and the relative proportions of the slow and fast tumbling components within the temperature range of $340 < T \leq 365$ K strongly suggest the presence of a bicontinuous spatial distribution of domains of the slow and fast reorienting $NO_3^-$ ions. Although a distribution of correlation times resulting from density or structural fluctuations in liquids may give rise to spatial heterogeneities within the $\alpha$ or $\beta$ processes, no definitive evidence of bimodality in these distributions in ionic liquids has been reported so far, to our knowledge. The fast and slow tumbling domains in CKN can be identified with the "liquidlike" and "solidlike" regions, respectively, as postulated in the free volume model coexisting near $T_g$ [9]. The rapid decrease in the fraction of the fast tumbling ions on cooling below 365 K is indicative of the increasing length scale of the slow domains or solidlike regions. Moreover, the similar time scales of $\tau_{shear}$ and the fast component $\tau_{NMR}$ indicate that motion in the liquidlike regions is responsible for the viscous flow in the supercooled liquid, as hypothesized also in the free volume model [9]. But our results do not show any evidence of a glass transition at the percolation threshold of the solidlike regions, as predicted in the free volume model.

As the average tumbling time scale in the slow domains is an order of magnitude longer than $\tau_{shear}$, the system is nonergodic at $T < 365$ K, in the time scale of $\tau_{shear}$. On the other hand, ergodicity is restored at $T > 365$ K as the domains of dynamical heterogeneity in CKN disappear at this temperature. It is tempting to identify this temperature $(T = 365$ K) with the mode-coupling transition temperature [1] or $T_c$. In fact, this value of $T_c$ corresponds quite well with that obtained $(T_c = 368 \pm 5$ K) from recent neutron scattering experiments [2121]. Such an identification of mode-coupling $T_c$ with the domain disappearance temperature was also suggested by Stillinger [2] in his domain tectonics model of glass transition. However, in this model, the two time scales differentiating the dynamics within the "domains" and the "domain walls" correspond to a slow $\alpha$ process and a fast

TABLE I. $^{15}$N line shape simulation parameters for CKN at different temperatures.

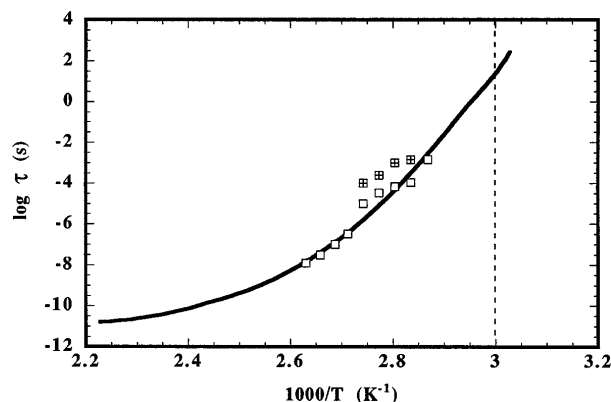| Temperature (K) | $\log_{10} \tau_{NMR}$ (s) | Fraction of the slow population |
|---|---|---|
| 1. 349 | $-2.84$ | ? |
| 2. 353 | $-2.84$ (slow) | 0.75 |
|  | $-3.98$ (fast) |  |
| 3. 357 | $-3.00$ (slow) | 0.58 |
|  | $-4.18$ (fast) |  |
| 4. 361 | $-3.60$ (slow) | 0.45 |
|  | $-4.48$ (fast) |  |
| 5. 365 | $-4.00$ (slow) | 0.40 |
|  | $-5.00$ (fast) |  |
| 6. 369 | $-6.48$ | $\cdots$ |
| 7. 372 | $-7.00$ | $\cdots$ |
| 8. 376 | $-7.51$ | $\cdots$ |
| 9. 380 | $-7.90$ | $\cdots$ |



FIG. 4. Comparison of the correlation time $\tau_{NMR}$ (open squares), with $\tau_{shear}$ (solid line, [13]) for CKN glass and liquid at different temperatures. For details see text. The slow component of $\tau_{NMR}$ is shown (crossed squares) in the temperature range where the dynamics is heterogeneous. The dashed vertical line marks $T_g$.

$\beta$ process, respectively, and not to a bimodality within the $\alpha$ process itself, as is observed here.

In summary, we have observed isotropic tumbling dynamics of $NO_3^-$ ions in the vicinity of the glass transition in the CKN liquid. The time scale of this dynamics corresponds very well with that of the $\alpha$ process. The tumbling dynamics becomes bimodally heterogeneous on cooling the CKN liquid below 365 K. The coexisting slow and fast populations of $NO_3^-$ ions change their relative proportions on cooling. These observations indicate the presence of spatial heterogeneity in the supercooled CKN liquid at $T < 365$ K, in the form of a bicontinuous distribution of slow and fast domains. The dynamics in the fast domains are responsible for the viscous flow, whereas the slow domains have lifetimes at least an order of magnitude longer than $\tau_{shear}$. The slow domains grow at the expense of the fast ones with decreasing temperature.

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