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New Microscopic Mechanism for Secondary Relaxation in Glasses

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The dynamics of simple molecular systems showing glassy properties has been explored by dielectric spectroscopy and nuclear quadrupole resonance (NQR) on the halogenomethanes CBr_2Cl_2 and $CBrCl_3$ in their low-temperature monoclinic phases. The dielectric spectra display features which correspond to α- and β-relaxation processes, commonly observed in canonical glass formers. NQR experiments, also performed in the ergodic monoclinic phase of CCl_4, enable the determination of the microscopic mechanism underlying the β dynamics in these simple model glasses: Molecules that are nonequivalent with respect to their molecular environment perform reorientational jumps at different time scales. Thus our findings reveal another mechanism that can give rise to typical β-relaxation behavior, raising some doubt about the existence of a universal explanation of this phenomenon.

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The glass transition in most glass formers, such as window glass or a wide variety of molecular systems, results from the freezing of translational and rotational degrees of freedom. These freezing processes display a temperature dependence of the characteristic relaxation times mimicking that of the macroscopic viscosity. A strikingly similar phenomenology is, however, also observed in systems in which the centers of mass of the molecules form a translational long-range-ordered lattice while the orientational degrees of freedom are thermally activated (termed rotator phases or plastic crystals, PCs) and which can be driven into a glassy crystal (GC) [1]. Such systems enable the study of the canonical liquid → glass transition alongside with that arising from the arrest of the rotational dynamics, i.e., PC → GC, and therefore have served as model systems to quantify the importance of translational and rotational degrees of freedom for glassy dynamics [2,3]. This has widened the concept of glassy dynamics to comprise systems varying from orientationally disordered crystals [1,2], colloids [4], and proteins [5] to a whole group of model systems [6]. An even simpler kind of glasses in which, although the molecular building blocks (tetrahedra in our case) form a crystalline lattice, the molecules perform large-angle molecular rotational jumps around molecular axis, are the scope of this work.

Several open questions remain to be settled concerning glass-forming materials and among those, the nature of features appearing within the generalized susceptibility spectra have been the focus of intense debates in the recent past [7]. Specifically, in the imaginary part of the susceptibility typical glass-forming materials display a strong peak dubbed as α-relaxation ascribed to processes involving liquid-flow, and a less-intense, higher-frequency relaxation, usually referred to as β-relaxation. This feature appears as well defined peak or shoulder at the high-frequency flank of the α-peak [7]. Its microscopic origin has been widely debated. The proposed explanations ascribe it either to intramolecular dynamics or to some sort of intrinsic dynamics characteristic of glass-forming materials.

Here we report on glassy dynamics of systems composed of globulelike molecules where the directional forces are far weaker than those due to excluded-volume interactions and therefore they constitute a system closer to those able to be explored by theoretical models [6]. The materials in question are the series of halogenomethanes CBr_nCl_{4-n}, $n = 0, 1, 2$. Calorimetrically, these materials exhibit a series of thermally induced solid-solid phase transitions that are attributed to the ability to thermally activate rotational degrees of freedom within the crystalline state. Such motional freedom results from weak intermolecular forces which allow reorientational processes to take place. In fact, cooling the melts leads to rotator phases which show translational fcc lattices ($Z = 4$) with carbon atoms sitting at the lattice nodes. Further cooling below 226, 238, and 259 K for CCl_4, $CBrCl_3$, and CCl_2Br_2, respectively, leads to a transformation into complex monoclinic, $C2/c$ structures with $Z = 32$ molecules per unit cell. Specific heat measurements within this phase [8] for $n = 1, 2$ bromochloromethane compounds revealed the existence of a glass transition (detailed analyses of the structural characteristics can be found in [9]).

The dynamics of these simple glassy systems, showing the freezing of reorientational jumps of molecules between crystallographic equilibrium positions, has been investigated by means of the concurrent use of dielectric and

nuclear quadrupole resonance spectroscopy (NQR) measurements. The first technique provides information about time correlations involving the macroscopic polarization, while the second allows us to follow the microscopic dynamics as sensed by the Cl nuclei. In doing so, we can also explore the dynamics of a material with very low polarization such as CCl_4. There, the isostructural low-temperature phase does not reveal any glass transition associated with the halogen atoms; i.e., the phase is ergodic (static and long-time averaging processes are equivalent), and thus in the present work it is taken as a reference. Some of these materials, especially those composed of molecules having high point-group symmetries (T_d, i.e., spherical tops) have been studied in quite a number of papers [10] whereas only a few preliminary experiments have been reported on those composed by particles with lower, C_{3v} or C_{2v}, symmetry ($CBrCl_3$ and CCl_2Br_2, respectively). Single crystal studies [11] on the structure of the low-temperature ordered phase of CCl_4 concluded that the asymmetric unit contains four nonequivalent molecules (i.e., using symmetry operations we need only these four molecules to reconstruct the unit cell). There are $Z = 32$ molecules per unit cell and within experimental uncertainty, all molecules are regular tetrahedra. Structural studies of the low-temperature phases of $CBrCl_3$ and CBr_2Cl_2 attempted by Binbrek *et al.* [11], using neutron powder diffraction experiments and lately confirmed [9], have unequivocally shown that in these monoclinic phases there is an intrinsic disorder with respect to the occupancy of the halogen sites. Large-angle rotations of tetrahedra around the symmetry axes of both compounds produce a statistical occupancy of 50% Cl and 50% Br atoms in the case of CCl_2Br_2 and of 75% Cl and 25% Br atoms for CCl_3Br.

$CBrCl_3$ and CCl_4 samples with purities of 99% and distilled CBr_2Cl_2 (initial purity of 98%) were employed. Dielectric measurements were performed using a frequency response analyzer (10 mHz $< \omega <$ 1 MHz) and an impedance analyzer (1 MHz $< \omega <$ 1.8 GHz) [12]. Temperature control of the samples was better than 0.1 K. Special gold-coated parallel-plate capacitors made of glass were used for measuring the small dielectric signal. ^{35}Cl NQR measurements were made using a home-made Fourier transform pulse spectrometer for CCl_3Br and CCl_2Br_2, and a Bruker MSL300 at zero field for CCl_4. The samples (ca. 1.5 g), were sealed under vacuum and their temperature controlled within 0.1 K. The NQR spectra for CCl_4 were obtained from the Fourier transforms of the free induction decay (FID). For the CCl_3Br and CCl_2Br_2 compounds, the reconstruction nuclear spin-echo Fourier transform mapping spectroscopy method was used [13]. The ^{35}Cl spin-lattice relaxation time T_1 was measured using the $\pi - \tau - \pi/2$ inversion recovery sequence. Because the rf pulses do not cover the whole line in CCl_3Br and CCl_2Br_2, the spin-lattice relaxation time T_1 in these compounds will reflect the relaxation of those ^{35}Cl nuclei with NQR frequencies near the center of the lines. The well-resolved lines of CCl_4 decay purely exponentially, whereas those for the substituted compounds show for temperatures 95 K $\leq T \leq$ 110 K a stretched exponential behavior with a stretching parameter between 0.8 and 0.9 which arises from the orientational disorder.

Figure 1 displays dielectric loss spectra for $CBrCl_3$ and CBr_2Cl_2 within the low-temperature monoclinic phase. As expected for a partially ordered solid, the dielectric strength is found to be very small. The main feature of the data shown in Fig. 1 is a well-defined α-like relaxation peak which continuously shifts towards lower frequencies with decreasing temperature and mimics the freezing of a canonical glassy system. For temperatures higher than $\approx$200 and 170 K for $CBrCl_3$ and CBr_2Cl_2, respectively, the loss spectra are well described by the Havriliak-Negami (HN) function with $0.1 < \alpha_{HN} < 0.4$ and $0.4 < \beta_{HN} < 0.8$. At lower temperatures, a shoulder (β relaxation) at the high-frequency tail shows up and a Cole-Cole (CC) function was added to the HN function to account for the more complex spectra. Furthermore, the high temperature spectra of CCl_2Br_2, even if not showing a β relaxation evident for the naked eye, could not be fitted using a single peak, revealing the existence of two distinct relaxation processes.

A sample of ^{35}Cl NQR spectra for the three compounds is shown in Fig. 2. Already at first glance, the striking difference between the well-resolved spectra for the ordered monoclinic phase of CCl_4 and the broad features

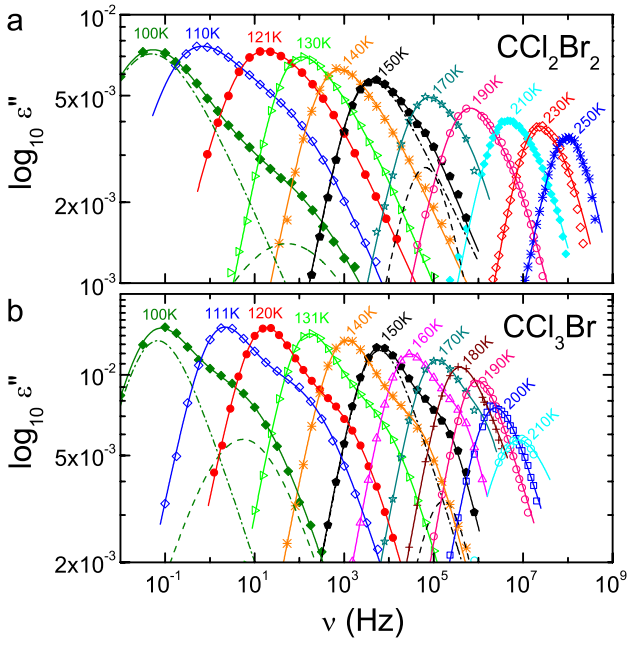

FIG. 1 (color online). Dielectric loss spectra of CBr_2Cl_2 (a) and $CBrCl_3$ (b) for a set of temperatures. The solid lines are fits using a Havriliak-Negami and a Cole-Cole function for the α and β processes, respectively. For two temperatures (100 K and 150 K) we show also the two separated relaxation processes, α and β, used for the construction of the function (for CBr_2Cl_2 the β process at 150 K was multiplied by a factor of 5 to make it visible at this scale).

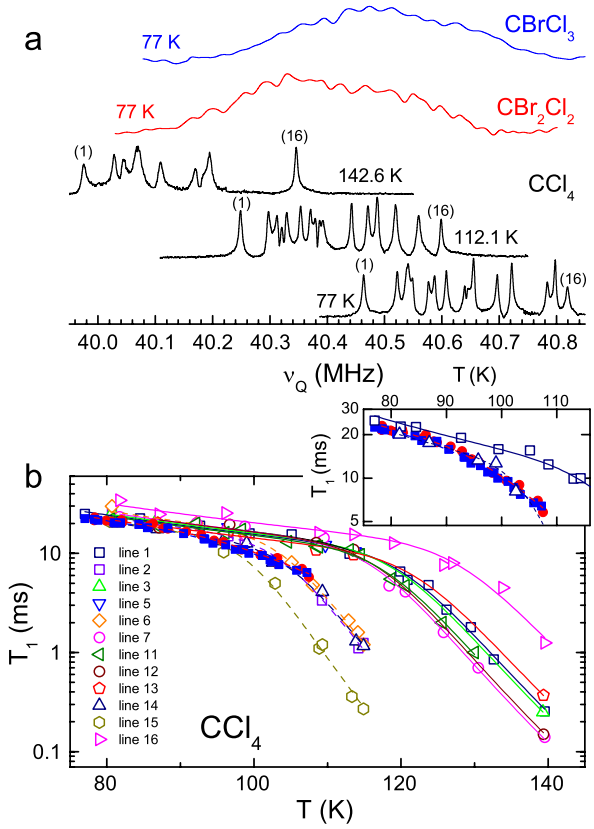

FIG. 2 (color online). (a) NQR spectra in the monoclinic phase for CBr_2Cl_2, $CBrCl_3$, and CCl_4 (for the latter, lines of independent ^{35}Cl atoms are consecutively numbered from 1 to 16). (b) Spin-lattice relaxation times (T_1) for CCl_4 (empty symbols), $CBrCl_3$ (full circles), and CBr_2Cl_2 (full squares), together with the fits using a phonon and reorientational contribution (see text). The solid (dashed) lines show fits for ^{35}Cl lines corresponding to the $\alpha(\beta)$ relaxation. The inset shows T_1 in more detail for $CBrCl_3$ and CBr_2Cl_2 lines together with two selected lines associated to the α (solid) and β (dashed) relaxations of CCl_4 for comparison.

appearing for the bromochloromethane compounds is revealed. CCl_4 spectra displays, between 77 and 120 K, 16 NQR lines with a broadening of 6 kHz, typical for ordered phases. They arise from the 16 nonequivalent Cl atoms of the 4 molecules forming the asymmetric unit as revealed by crystallographic studies [11]. Only 12 lines could be tracked over the whole temperature range due to overlaps and cross-overs of close frequency lines. At temperatures higher than 125 K, additional broadening develops due to fast dynamics. In stark contrast, only a single broad peak appears for the bromochloromethane compounds due to the disorder generated by halogen exchange.

Quadrupolar relaxation in symmetric molecular groups is due to two types of mechanism: A phonon contribution and slow reorientation jumps of the molecules ($\omega_{NQR}\tau_{reor} \gg 1$) between equivalent positions [14]. The relaxation rates for each nucleus that participates in the reorientation can be described by the sum of these two independent processes [14,15]:

$$T_1^{-1} = (T_1^{-1})_{phonon} + (T_1^{-1})_{reor} = AT^2 + 3/2\sum_{\nu'}(1 - \cos^2\theta_{\nu\nu'})W_{\nu\nu'} = AT^2 + 3/4\tau_{reor}^{-1}(T), \quad (1)$$

where $\theta_{\nu\nu'}$ are the tetrahedral angles of the molecules, and $W_{\nu\nu'}$ are the jump probabilities between sites ν and ν', which, following [14], can be related to the relaxation times by $\tau_{reor}^{-1} = \sum_\mu W_{\nu\mu}$.

The reorientational contribution to the relaxation process τ_{reor}, which is the main contribution to T_1 at high temperatures, can be therefore extracted from the data. The relaxation times as a function of temperature, derived for dielectric as well as NQR techniques, for all compounds are well accounted for by an Arrhenius equation, which makes these materials classifiable as strong glasses using the Angell criterion (Fig. 3).

Let us focus now on data for CCl_4, for which the absence of any dipole moment prevents the determination of the dielectric response. The temperature dependence of the relaxation times is plotted in Fig. 3. The data shown there display two well separated processes with times differing by about a decade. To ascertain that they arise from different molecules and are not due to different motions of a single molecule, we have calculated the limiting dynamics

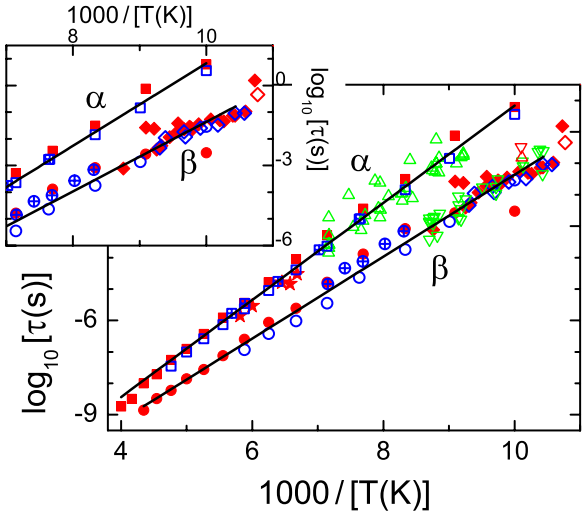

FIG. 3 (color online). Relaxation times obtained for the three studied compounds: Squares for the α and circles for the β relaxation for CBr_2Cl_2 and $CBrCl_3$ (full and empty, respectively), symbols with crosses are those obtained from the literature [16] for $CBrCl_3$ and stars are those for CBr_2Cl_2. Diamonds are reorientational correlation times obtained from NQR measurements (as before full and empty for CBr_2Cl_2 and $CBrCl_3$, respectively) and triangles are those for CCl_4, triangles up associated with α relaxation and triangles down associated with β relaxation. Lines are fits for both processes α and β with activation energies $E_\alpha = 0.31$ eV and $E_\beta = 0.26$ eV. Results only showing relaxation times obtained for CBr_2Cl_2 and $CBrCl_3$ are shown in the inset for the low-temperature region.

that would result in the latter case. For this purpose, we have used the aforementioned relationship between τ_{reor} and the probability jump between sites ($W_{\nu\nu'}$) which take place by means of reorientations about the four C_3 and three C_2 molecular axes. In addition, we took into account that there are at least 8 lines with the longest correlation times (see Fig. 2). From this, we obtain a maximum ratio between the slow and fast movements of $\tau_{fast}/\tau_{slow} = 2$, which is clearly disparate from the ratio experimentally observed ($\tau_{fast}/\tau_{slow} \approx 30$).

Other feasible origins for these two dynamical processes as, e.g., a large-angle molecular reorientational jump about some molecular symmetry axis plus a librational movement, are also discarded since libration mechanisms would not be able to yield a huge decrease in $T_1(T)$ as that shown in Fig. 2 [14,15]. Therefore, based on the experimentally obtained ratio of NQR lines describing fast or slow motions, the dynamics present in CCl_4 must be associated to the slower dynamics of one molecule and the faster dynamics of the other nonequivalent three in the asymmetric unit. Astonishingly enough, the slow (α) and fast (β) processes for the bromochloromethane compounds displaying a glassy behavior in the monoclinic phase, take place at the same time scale and with activation energies close to those of the nonequivalent molecules in the ordered monoclinic phase of CCl_4. The current results are also in line with those reported by Yamamuro *et al.* [16] where the suggestion of relating the observed two relaxation phenomena to motions of nonequivalent molecules within a crystal lattice, is also made.

In summary, we have studied the dynamics of a very simple type of glass former, where strongly restricted reorientational motions in a long-range ordered crystalline lattice becomes frozen. The dielectric spectra display two relaxation processes α and β; i.e., these materials exhibit the typical phenomenology of canonical glass formers. In the work of Johari and Goldstein [17], where secondary relaxations in a number of structural glass formers composed of rigid molecules were studied, they were shown to be ''a universal feature of the glassy state''. Nowadays, such relaxations, not arising from intramolecular degrees of freedom, are termed Johari-Goldstein β-relaxations. The most commonly considered microscopic mechanisms to explain this phenomenon are ''islands of mobility'', i.e., regions with lower density and, thus, faster molecular dynamics [17,18], or small-angle reorientations performed by all molecules [19]. In the present work, secondary relaxations in rigid molecules are detected, too. However, for these simple glasslike materials, a different picture evolves: The two relaxations arise from the different dynamics exhibited by molecules in the asymmetric unit of the crystalline lattice that are nonequivalent with respect to their molecular environment. Therefore, while β relaxations are a universal feature of the glassy state [17,20], there seems to be no universal microscopic mechanism describing them.

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