# Nonresonant Spectral Hole Burning in the Slow Dielectric Response of Supercooled Liquids

## B. Schiener, R. Böhmer,* A. Loidl,† R. V. Chamberlin*

Large-amplitude, low-frequency electric fields can be used to burn spectral holes in the dielectric response of supercooled propylene carbonate and glycerol. This ability to selectively modify the dielectric response establishes that the non-Debye behavior results from a distribution of relaxation times. Refilling of the spectral hole was consistent with a single recovery time that coincided with the peak in the distribution. Moreover, refilling occurred without significant broadening, which indicates negligible direct exchange between the degrees of freedom that responded to the field. Nonresonant spectral hole burning facilitates direct investigation of the intrinsic response of systems that exhibit nonexponential relaxation.

When subjected to an external perturbation, many materials, including polymers (1), proteins (2), and supercooled liquids (3), exhibit nonexponential relaxation. The response of thousands of different substances (4) has been characterized by the Kohlrausch-Williams-Watts (KWW) stretched exponential, $\exp[-(t/\bar{\tau})^{\beta}]$, where $\beta < 1$, $t$ is time, and $\bar{\tau}$ is a characteristic relaxation time. It has long been debated (5–8) whether this dynamical complexity is intrinsic, with all regions of the sample exhibiting a similar non-Debye response, or whether it is the result of heterogeneity, with localized degrees of freedom relaxing exponentially but with a distribution of relaxation times that yields the net behavior. Several studies (9–11) of supercooled liquids near their calorimetric glass transition temperature $T_g$ have concluded that heterogeneity occurs on length scales of 1 to 5 nm. Recent magnetic resonance measurements (12) have shown that these domains are not static, but that their distinct relaxation rates persist long enough to cause the broadened response. Such dynamic heterogeneity, which evolves as the sample responds, has not previously been observed directly in the slow dielectric response.

Spectral hole burning (SHB) may be the most direct technique for investigating the constituents in the net response of a macroscopic sample. Observation of SHB generally requires a heterogeneously broadened spectrum, a strong external signal that can modify selected parts of the spectrum, and a resulting "hole" that is persistent enough to allow subsequent measurement of the modified response. An important advantage of the technique is that the responding de-
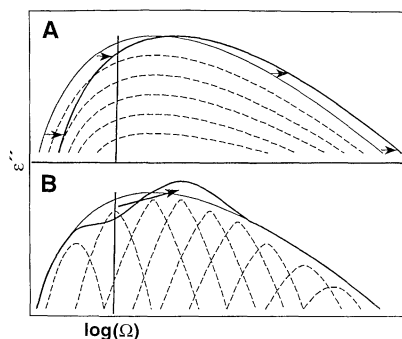
grees of freedom are used directly as their own local probe. SHB was first observed in magnetic resonance spectroscopy (13, 14) but is now most commonly applied to optical resonances (15) by means of the intense monochromatic fields available with modern lasers. Here, we report direct measurements of dielectric SHB in nonresonant relaxation.

The basic idea of nonresonant SHB (NSHB) in supercooled liquids is easiest to picture in the context of dielectric loss $\varepsilon''$ as a function of frequency (Fig. 1). Observed loss peaks are generally broader than that of a simple Debye response. According to the Boltzmann superposition principle (16), linear macroscopic measurements cannot distinguish between intrinsic broadening (Fig. 1A) or a distribution of response times (Fig. 1B). Although nonlinear saturation of the dielectric polarization in a static field is usually precluded by dielectric breakdown, dielectric heating in an oscil-



**Fig. 1.** Sketch of the dielectric loss as a function of logarithm of frequency from the intrinsic degrees of freedom in a sample exhibiting (**A**) homogeneously broadened response and (**B**) response resulting from a distribution of relaxation times. In (A), when a pump field is applied at frequency $\Omega$, energy is absorbed homogeneously, yielding a uniform shift in the spectrum of response. In (B), however, domains with absorption at $\Omega$ are selectively modified, and a spectral hole develops.

lating electric field (which is quadratic in the amplitude of the field) can be used to modify the frequency of response. If energy from the field were absorbed homogeneously (Fig. 1A), the entire spectrum would simply be shifted to higher frequencies, whereas in the case of a heterogeneous response (Fig. 1B), the energy absorbed would depend on the local response, and a spectral hole would develop. If the excess local energy simply heated the thermal bath, it would diffuse out of a typical domain (assuming diameters of $\leq 5$ nm) in less than a nanosecond. Instead, we have found that local modifications induced by the electric field persist long enough to reveal the heterogeneity in the slow relaxation and to be observed with time-domain spectroscopy.

To measure time-dependent dielectric polarization, we used a Sawyer-Tower bridge (17) consisting of a parallel-plate sample capacitor and an integrating capacitor connected in series across a computer-controlled high-voltage supply. The distance $d$ between the sample plates was maintained at 50 μm with quartz fibers, yielding a nominal empty-cell capacitance of 30 pF. The sample capacitor was immersed in the dielectric liquid, whose temperature was controlled by a closed-cycle refrigeration system to an absolute accuracy of $\pm 1$ K, with a relative stability of $\pm 3$ mK. A high-impedance amplifier was used to monitor changes in voltage across the integrating capacitor, which are proportional to changes in the polarization of the sample.

To measure NSHB, we devised a pump-and-probe procedure that combines the frequency selectivity of an oscillating field with the advantages of inducing the entire spectrum of time-dependent response after a single step in the applied field (Fig. 2). A sinusoidal pump voltage of amplitude $V_0$ and frequency $\Omega$ was used to selectively modify the sample. After a recovery time $t_r$, a probe step of amplitude $+v$ was applied, yielding the time-dependent polarization of the locally modified sample $P_+^*$. The large but uninteresting linear response from the pump field was removed by means of a phase-cycling technique in which an identical pump oscillation and recovery time is followed by a negative probe step $-v$, yielding $P_-^*$. The difference $P_+^* - P_-^*$ is proportional to the transient dielectric permittivity $\varepsilon^*(t)$ of the locally modified sample, which can be compared with the usual bulk response $\varepsilon(t) \propto P_+ - P_-$. Another advantage of the phase-cycling procedure is that it removes all extrinsic nonlinear effects from the pump oscillation (18); such effects often interfere with the intrinsic nonlinear dielectric response when measured by conventional techniques (19). The results we report occurred reproducibly in the raw

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data, but because of occasional slight temperature drifts, some of the data have been corrected by a small factor (<0.1%) times the response from the pump field ($P_+^*$ + $P_-^*$).

Most data shown here are for propylene carbonate (PC), which was chosen for its extraordinarily large dielectric loss and highly temperature-dependent relaxation rate near $T_g \sim 156$ K (20). We also studied glycerol, which has a smaller dielectric loss and less pronounced temperature dependence near its $T_g$ of 190 K and exhibits weaker but otherwise similar NSHB behavior. Figure 3 shows NSHB in PC taken at a temperature $T$ of 157.4 K. Close inspection of the raw data (Fig. 3A) reveals that the 2-Hz oscillation modified the spectrum most at short times, whereas the 0.01-Hz oscillation modified the spectrum most at long times. The result is amplified by taking the difference in the dielectric permittivity at each time $\Delta\varepsilon(t)$ (Fig. 3B); this shows that the response that is modified most by the 2-Hz oscillation is virtually unchanged by the 0.01-Hz oscillation, and vice versa. Such segregated response clearly establishes the heterogeneous nature of the dielectric loss. Near $T_g$, PC has a relatively narrow distribution of relaxation times, with a net spectrum of response from bulk samples that is only 1.3 times the Debye width. Still, the spectral hole is significantly narrower than the net response, which indicates that the intrinsic local response is effectively single exponential.

A more physically meaningful way to show how the pump oscillation has changed the relaxation times of the responding degrees of freedom is to plot the change in the logarithm of the relaxation times as a function of time $\Delta(t)$, as defined in the inset of Fig. 3A. If the response were homogeneous, the response rates of all domains would be modified uniformly, yielding a constant value for $\Delta(t)$. Instead, different frequencies are found to modify different parts of the spectrum (Fig. 3C). This result provides a direct demonstration that the slow dielectric relaxation was heterogeneously broadened.
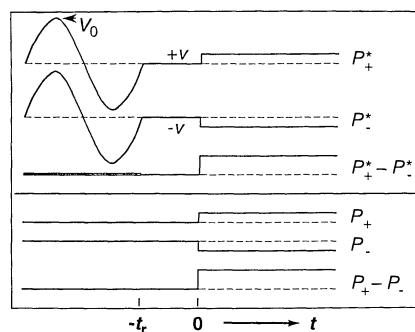
We have modeled the observed behavior assuming that the sample contains discrete domains that relax exponentially according to $\exp(-t/\tau_i)$, with each distinct relaxation time $\tau_i$ enumerated by index $i$. The distribution of relaxation times $g_i$ was determined empirically by fitting the net unmodified response $\sum_{i=1}^{\infty} g_i \exp(-t/\tau_i)$ to the measured bulk response $\varepsilon(t)$; these same $g_i$ were then used to characterize the spectral hole. NSHB involves adding energy to selected domains, thereby selectively modifying their local response rates. As noted above, thermal diffusion would prevent observation of NSHB if the induced energy immediately flowed into the thermal bath. Therefore, the energy must persistently modify the

local dynamics, possibly by modifying the density (21) or size (9, 22, 23) of the selected domains, which may be described in terms of a local fictive temperature $T_{f,i}$ (24). In ergodic liquids, the fictive temperature is equal to the thermodynamic temperature, but quenched samples often exhibit aging in their response as the fictive temperature approaches $T$. Over the temperature range of our study, changes in relaxation times may be approximated by an Arrhenius law, $\tau_i \propto \exp(B/T_{f,i})$, which for bulk fictive temperature is known as the Narayanaswamy-Moynihan equation. We assume a uniform effective energy barrier $B$, which is determined empirically from temperature dependence of the characteristic relaxation time $\bar{\tau}$. Thus, for small changes in local fictive temperature, changes in the local relaxation times may be written as $\Delta\ln(\tau_i) = (-B/T^2)\Delta T_{f,i}$.

After $N$ oscillations of an electric field of amplitude $E$ and frequency $\Omega$, the total heat absorbed in a system characterized by dielectric loss

$$\varepsilon_i'' \propto \frac{\Omega\tau_i}{1 + (\Omega\tau_i)^2} \qquad (1)$$

is $Q_i = N\pi\varepsilon_0\varepsilon_i''E^2$, where $\varepsilon_0$ is the permittivity of free space. If all this heat remained in the individual domains that absorbed the energy, their local fictive temperatures would increase by $\Delta T_{f,i} = Q_i/\Delta c_p$, where $\Delta c_p$ is the specific heat of the responding degrees of freedom (which can be deduced from the difference in $c_p$ from above and below $T_g$). For PC with $T_f \approx T_g \approx T = 157.4$ K, $\Delta c_p = 7.7 \times 10^5$ J m$^{-3}$ K$^{-1}$ and $B/T_g = 230$ (20). The internal field induced by the pump voltage is influenced by depolarizing effects. We used the Lorentz formula for spherical domains in a thin

sample between parallel plates, $E = (V_0/d)$ $(\varepsilon' + 2)/3\varepsilon'$, where the net in-phase dielectric response is

$$\varepsilon' = \sum_{i=1}^{\infty} \frac{g_i}{1 + (\Omega\tau_i)^2} + \varepsilon_\infty \qquad (2)$$

with $\varepsilon_\infty \approx 5$. There are no adjustable parameters in this model. The good agreement with the observed spectral holes (Fig. 3C) therefore provides quantitative evidence that NSHB in PC involves local dielectric heating. Discrepancies between calculated and observed behavior, especially after the 0.01-Hz modification, result mainly from recovery mechanisms in the sample, as discussed below.

We found that spectral modification was more strongly dependent on the power than on the energy from the electric field. The size of the spectral hole increased quadratically with increasing field amplitude (Fig. 4), indicating linear dependence on the power from the pump oscillation. However, the size of the spectral hole saturated with
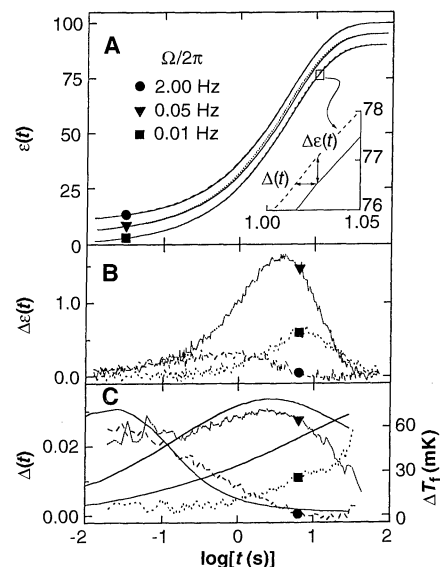


**Fig. 3.** (**A**) Time-dependent dielectric permittivity of PC at 157.4 K. Solid curves are the unmodified response; dashed curves are the response after modification by a single oscillation of 900 V at 2.00 Hz (upper curves), 0.05 Hz (middle curves), and 0.01 Hz (lower curves). The upper and lower pairs of curves are offset for clarity. Results obtained from the data of (A) [as shown in the inset of (A)] are presented in (**B**), the difference between modified and unmodified dielectric permittivities, and (**C**), the difference in the logarithm of the relaxation times at each time point. In (C), homogeneously broadened response would yield horizontal lines. The smooth curves in (C) were calculated from a distribution of relaxation times with no adjustable parameters. Discrepancies, most visible after the 0.01-Hz pump oscillation, are mainly a result of neglecting recovery effects.



**Fig. 2.** Voltage sequences that yielded modified $(P_+^*, P_-^*)$ and unmodified $(P_+, P_-)$ time-dependent polarizations. For the data reported here, the amplitude of the probe step was $+v = 150$ V. Unless otherwise indicated, the amplitude of the pump oscillation was $V_0 = 900$ V. Care was taken to allow full recovery of the sample after each relaxation. If not for dielectric heating during the pump oscillation, the differences $P_+^* - P_-^*$ and $P_+ - P_-$ would be identical.

increasing oscillations at fixed amplitude, indicating that energy flowed out of selectively heated domains during their response. NSHB, where measurements are made as energy flows out of the selectively heated domains to the thermal bath, is therefore consistent with specific heat spectroscopy (25, 26), where measurements are made as energy flows from the thermal bath to the slow degrees of freedom.

The spectral hole refilled as a function of the recovery time ($t_r$) as the locally modified relaxation times returned to their ergodic distribution (Fig. 5). Although similar to traditional bulk aging experiments (27), NSHB has some distinct advantages. First, the minimum time for measuring a modified spectrum is limited only by the speed of the high-voltage supply, not a thermal quench rate. Our apparatus has a minimum $t_r$ of ~2 ms, allowing local aging experiments at temperatures above $T_g$. NSHB also provides details about spectral shape during recovery, and specific constituents can be emphasized by changing the frequency at which the

sample was modified. Within experimental resolution, all parts of the sample recover at the same rate $\gamma$, and this recovery rate is independent of the pump frequency $\Omega$. Moreover, the general shape of the spectral hole is preserved during recovery (Fig. 5), which indicates that the locally modified domains do not significantly modify their neighbors. Thus, on the time scale of the response, direct exchange between domains does not have to be taken into account.

The distribution of relaxation times in the linear dielectric response was compared with the single recovery rate of spectral hole refilling (Fig. 6). Assuming $\Delta_{max} \sim \exp(-\gamma t_r)$, we obtained $\gamma = 0.083$ s$^{-1}$ and 4.2 s$^{-1}$ for PC at 161.0 and 157.6 K, respectively, and $\gamma = 0.73$ s$^{-1}$ for glycerol at 194.7 K. Characteristic relaxation times for the linear response $\bar{\tau}$, which for these liquids are within about 10% of the peak in the distribution (28), are 0.082 and 4.1 s for PC at 161.0 and 157.6 K, respectively, and 0.71 s for glycerol at 194.7 K. Such similar values for $\bar{\tau}$ and $1/\gamma$ may be contrasted with the photobleaching of probe molecules in orthoterphenyl (11), where an average probe molecule must rotate more than 100 times before the equilibrium distribution of rotation rates was recovered. Our measurements indicate relatively fast recovery of the ergodic distribution of relaxation times in PC and glycerol, possibly explaining why traditional aging experi-

ments have never been reported for these substances.

We have shown that a pump-and-probe procedure can be used for SHB in the nonresonant dielectric response of supercooled liquids. The procedure could also be applied to other techniques—such as magnetometry, viscoelastometry, or photon correlation spectroscopy—on any system that exhibits nonexponential relaxation.

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18. The only modification induced by the pump oscillation that changes sign between positive and negative probe steps is the intrinsic dielectric response. Thus, all extrinsic nonlinear effects resulting from the pump oscillation—such as electrode polarization, sample electrostriction, and viscoelastic deformation of the capacitor geometry—are completely eliminated by phase cycling. Although nonlinear effects induced during the probe step are not removed, they are immeasurably small, and further reduced by a factor of $(+v/V_0)^2 = 1/36$, compared with the intrinsic heating from the pump oscillation.
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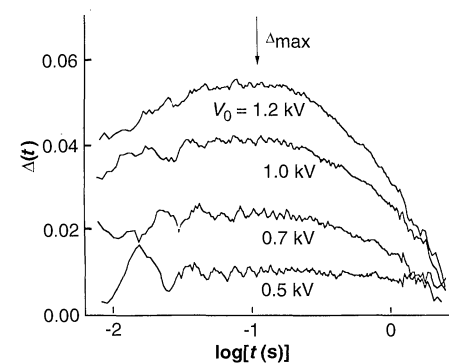
**Fig. 4.** Time-dependent modification of the relaxation times in PC at 159.6 K after a 1-Hz oscillation with various amplitudes $V_0$. When $V_0$ was doubled, from 0.5 to 1.0 kV, $\Delta(t)$ quadrupled. An accurate value for each maximum spectral hole size $\Delta_{max}$ was obtained by fitting to several points in the spectrum near the maximum modification (arrow), yielding $\Delta_{max} = 4 \times 10^{-8} V_0^2$.
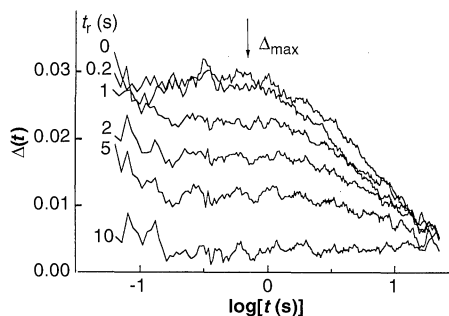


**Fig. 5.** Time-dependent modification of the relaxation times in PC at 157.6 K after a 0.2-Hz pump oscillation for various recovery times. Each value of $\Delta_{max}$ was obtained from several points in the spectrum near the maximum modification (arrow).
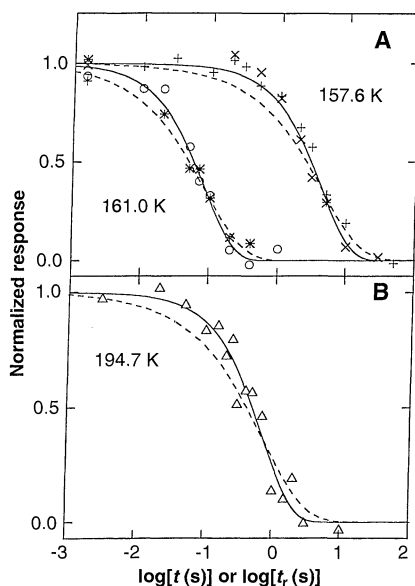


**Fig. 6.** Normalized dielectric relaxation as a function of time $[\varepsilon(\infty) - \varepsilon(t)]/[\varepsilon(\infty) - \varepsilon(0)]$ (dashed curves) and $\Delta_{max}$ as a function of recovery time (symbols) for (**A**) PC at 161.0 and 157.6 K and (**B**) glycerol at 194.7 K. Symbols are for recovery after modification by 10 Hz (∗), 1 Hz (○), 0.3 Hz (×), 0.06 Hz (+), and 0.5 Hz (△). Solid curves are the best single-exponential fits to the symbols that characterize spectral hole refilling.