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On the features of the dielectric response of supercooled ethylcyclohexane

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The main relaxation observed in supercooled ethylcyclohexane in the 50 Hz – 20 kHz frequency range using high-resolution dielectric spectroscopy displays an unusual relaxation pattern. The slope of the dielectric loss profile above the peak frequency progressively tends to zero with increasing temperatures. The observed features could be compatible with the existence of different underlying processes. This work exploits a simple approach based on scaling and provides relevant information on the properties of the primary and secondary relaxation in ethylcyclohexane. We show that the apparently anomalous behaviour is due to the superposition of a secondary process to the dielectric α -process and support the thesis that the β -relaxation observed in the glassy phase could have an intramolecular origin.

1. Introduction

Some interesting features of the dynamics of ethylcyclohexane (ECH) have been recently revealed using high-resolution dielectric spectroscopy [1] and mechanical spectroscopy at ultrasonic frequencies [2]. In fact ultrasonic measurements have provided evidence of the existence of two secondary relaxations, the γ -process and the χ -process, *slower* than the structural relaxation at temperatures above the glass transition region. Both relaxations have been ascribed to an intramolecular origin, and corresponding processes have been observed with closely similar Arrhenius behaviour in different materials (liquids, glasses, polymers, or dilute solutions in polymeric glassy matrices) having in common the presence of the cyclohexyl ring in their molecular structure. On the other hand, a secondary (β -) process *faster* than the α -relaxation has been revealed by dielectric spectroscopy in the glassy phase of ECH [1]. The temperature dependence of the peak frequency closely corresponds to the Arrhenius behaviour of the mechanical χ -process, extrapolated from temperatures typical of the ergodic liquid down to the calorimetric glass transition temperature and further below. On this basis the secondary dielectric β -relaxation could be supposed to share the same origin as the intramolecular χ -process, that would occur across the glass-transition with unaltered activation energy and prefactor. Nevertheless, the properties of the dielectric β -relaxation are reminiscent of the general behaviour of the so-called Johari-Goldstein (JG) secondary relaxation [3,4,5], with intermolecular character, that occurs in a wide variety of

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glass forming materials [6,7]. In addition to the facts mentioned above, it has been recently pointed out that the main dielectric relaxation in a temperature region corresponding to the deeply supercooled liquid, could be described using the phenomenological Havriliak-Negami (HN) equation

$$\varepsilon^*(\nu) = \varepsilon_{\infty} + \Delta\varepsilon \left[1 + (i 2\pi\nu\tau_{HN})^{\alpha} \right]^{-\gamma}, \quad (1)$$

with $\alpha \cong 0.90$ and quite low values (0.2 – 0.1) for the parameter γ , which accounts for the asymmetric broadening of the loss peak towards high frequencies. Such behaviour appears quite unusual for non-polymeric low-molecular-weight glass formers. In fact, very broad relaxation peaks, corresponding to low values of the stretching exponent β_{KWW} for the Kohlrausch-Williams-Watts (KWW) response function in the time domain, are mainly observed in liquids characterized by a high kinetic fragility [8] as in the case of neat decalin [9]. Instead, the estimated fragility of ECH [1] corresponds to the intermediate character of molecular liquids, as found for some alcohols and polyols [10]. Moreover, the HN parameter γ tends towards zero as the temperature increases. These aspects would suggest that the unusual shape of the main dielectric relaxation peak is due to the existence of concurring relaxational contributions. In order to get additional insight on the features of the dielectric response of ECH the dielectric spectra of the deeply supercooled liquid have been analyzed in this work starting from a test of the scaling properties. The results obtained with this approach reconcile the behavior of ECH with the common dynamical properties of glass forming liquids and support the conclusion that the dielectric β -relaxation observed in the present case is not a Johari-Goldstein relaxation.

2. Experimental

Dielectric measurements were performed using an ultra-high precision capacitance bridge Andeen-Hagerling AH 2700A in the frequency range 50 Hz – 20 kHz and a home made capacitance cell [1, 11]. The measurements were performed isothermally at selected temperatures in the range 300 K – 25 K, cooling from the liquid to the glassy state with a Leybold closed cycle helium refrigerator (RDK 6-320/Coolpak 6200), coupled to a LakeShore 340 temperature controller. The samples (Aldrich, purity > 99 %) were distilled twice prior to the measurement in order to minimize the influence of impurities on the dielectric spectra. The thermodynamic properties as well as the glass-forming ability of ECH were previously investigated by adiabatic calorimetry [12]: the glass transition occurs at 104.5 ± 1 K, for moderate cooling/heating rates (0.2 – 0.5 K/min); the melting temperature is 161.5 K.

3. Results: analysis and discussion

The dielectric loss ε'' of supercooled ethylcyclohexane is shown in figure 1 as a function of frequency in the range 50 Hz – 20 kHz at selected temperatures. Notwithstanding that this is the main dielectric relaxation associated with the structural α -process, its intensity is low: typical peak values of the imaginary permittivity are of about 3×10^{-3} . For this reason the dielectric response of this material could not easily be investigated with usual experimental equipment for broadband dielectric spectroscopy. As can be seen from figure 1, the dielectric loss peak becomes broader on the high frequency side with increasing

temperatures, and the apparent slope at frequencies higher than the maximum approaches zero (see for instance the experimental data set at 119 K).

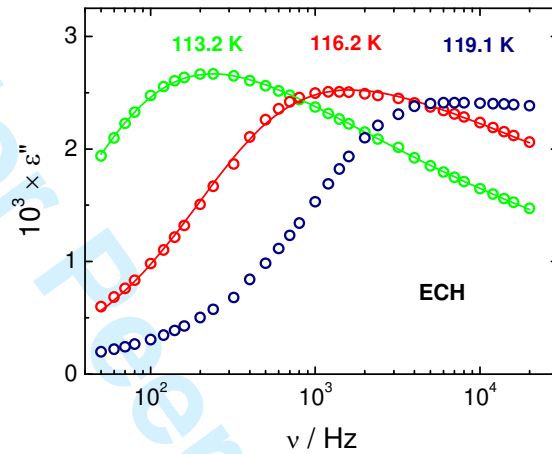


Figure 1. (Color online) Frequency dependence of the dielectric loss ε'' for the main dielectric relaxation in distilled ECH at selected temperatures. Solid lines correspond to the best fit of the Havriliak-Negami equation to the experimental data.

The construction of a master curve of $\varepsilon''/\varepsilon''_{\max}$ vs. ν/ν_{peak} has been attempted using the experimental dielectric spectra at temperatures between 111 K and 121 K (figure 2). Suitable initial estimates of ε''_{\max} and ν_{peak} were obtained by direct inspection of the experimental spectra at each temperature, then the refined value of ν_{peak} providing the best superposition with the master data set was selected. However, aiming to apply the same scaling procedure also to the experimental data at temperatures for which the peak is shifted out of the frequency range available, an extrapolation of the behaviour of ν_{peak} and ε''_{\max} as a function of temperature has been considered. The temperature dependent behaviour of the peak frequency is well described by a Vogel-Fulcher-Tammann (VFT) equation

$$\log_{10}(\nu_{\text{peak}}/\text{Hz}) = A' - \frac{B'}{T - T_0}, \quad (2)$$

with $A' = 12.9 \pm 0.3$, $B' = 397 \pm 27$ K, and $T_0 = 75.5 \pm 1.3$ K. These parameters correspond to a 'dynamic' glass transition temperature $T_g \cong 101$ K, estimated using the criterion $\tau_{\text{peak}}(T_g) = 100$ s. Deviations from the VFT behaviour of the supercooled liquid would be expected when the material is driven below the glass transition temperature [13,14]. Therefore the extrapolation of ν_{peak} and the construction of the master curve was limited to a temperature range in which the liquid could be considered at equilibrium during the measurement. On the other hand, in order to account for the temperature dependence of ε''_{\max} , the observed trend of ε''_{\max} vs. T has been modelled using a second order polynomial

$$y = c_0 + c_1x + c_2x^2, \quad (3)$$

with $c_0 = (4.5 \pm 0.3) \times 10^{-2}$, $c_1 = -(6.8 \pm 0.5) \times 10^{-4}$, and $c_2 = (2.7 \pm 0.2) \times 10^{-6}$. With this method the scaling has been extended to lower temperatures, down to 103 K, and to higher temperatures, up to 125 K. The corresponding peak frequency would span over about four decades.

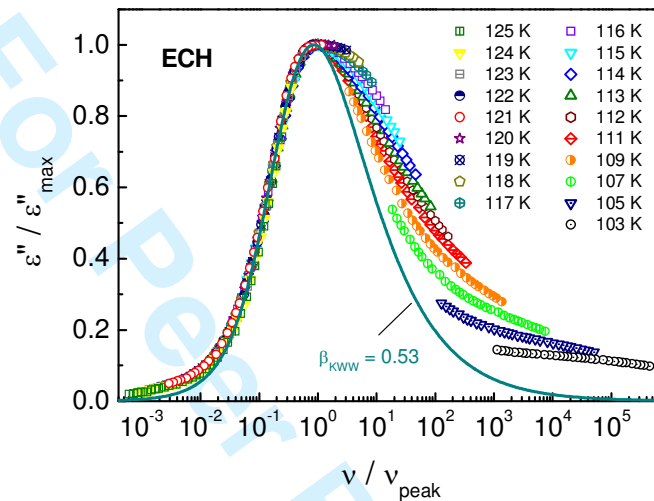


Figure 2. (Color online) Frequency-dependent dielectric loss $\varepsilon''/\varepsilon''_{\max}$ vs. ν/ν_{peak} of ECH obtained by normalizing the experimental data in the 103 K – 125 K temperature range. The solid line represents the numerical Fourier-transform of a KWW function with exponent $\beta_{\text{KWW}} = 0.53$.

From figure 2 it appears that all the spectra collapse on to a common line in the low frequency flank of the peak whereas differences occur on the high frequency side. The master plot in figure 2 might reflect the fact that: (i) a time-temperature superposition holds for the α -relaxation process in the vicinity of the glass transition temperature [15,16,17,18], and (ii) the deviations from an ideal master curve on the high frequency side of the peak are due to the role of the secondary β -relaxation. The spectral separation between the secondary process and the α -peak becomes larger at lower temperatures. In order to account for the main contribution, the numerical Fourier transform of the Kohlrausch-Williams-Watts (KWW) phenomenological equation in the time domain has been considered [19],

$$\varepsilon'' = \Delta\varepsilon \cdot \text{Im} \left\{ \int_0^{\infty} dt e^{-i2\pi\nu t} \left[-\frac{d}{dt} \exp \left[-\left(\frac{t}{\tau_{\alpha}} \right)^{\beta_{\text{KWW}}} \right] \right] \right\} \quad (4)$$

The frequency-dependent behaviour of the imaginary permittivity corresponding to a value $\beta_{\text{KWW}} = 0.53$ for the stretching parameter is shown for comparison in figure 2: this curve describes successfully the low-frequency side of the peak and the region close to the maximum. It should be noted that if the α -relaxation and the secondary β -relaxation were statistically independent processes, also the low-frequency side of the main peak in figure 2

could involve a contribution from the secondary β -relaxation, especially at higher temperatures. For this reason the actual value of β_{KWW} associated with the true α -relaxation might also be larger. Nevertheless the possible influence of the secondary relaxation apparently is not relevant enough to produce large temperature-dependent deviations from the master curve on the low-frequency side of the peak. Thus the set of scaled data has been exploited to simulate the missing part of the dielectric loss profile at each of the temperatures investigated, as shown in figure 3. The resulting pattern, for instance at 103 K, is compatible with the frequency-dependent permittivity obtained as the sum of two independent contributions: a main relaxation corresponding to the α -process, described by a KWW response as in equation (4), and a secondary relaxation described using a Cole-Cole equation

$$\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (i2\pi\nu\tau_{\text{CC}})^{\alpha_{\text{CC}}}} \quad (5).$$

The best agreement between the model equation and the 'extended' spectrum at 103 K was achieved for $\beta_{\text{KWW}} = 0.53 \pm 0.02$ and $\alpha_{\text{CC}} = 0.28 \pm 0.03$. At higher temperatures the secondary process does not appear as a separate feature, but it essentially influences the shape of the spectra at frequencies above the α -peak. For this reason the α -relaxation apparently broadens, but the same values of β_{KWW} provided the best description of the dielectric loss profile up to 111 K, in correspondence with average values of α_{CC} slightly increasing from 0.28 to 0.34 at increasing temperatures.. According to these findings, the results are compatible with the validity of a time-temperature superposition for the α -relaxation process. The values of the shape parameter concerning the secondary relaxation are larger, although still comparable with, those ($\alpha_{\text{CC}} = 0.17 \pm 0.01$) obtained from the analysis of the dielectric spectra acquired in the glassy phase [1]. In fact, the width of the secondary relaxations observed as processes faster than the α -relaxation, usually increases on decreasing the temperature [20]. The comparison between simulated and experimental spectra at different temperatures is shown in figure 3.

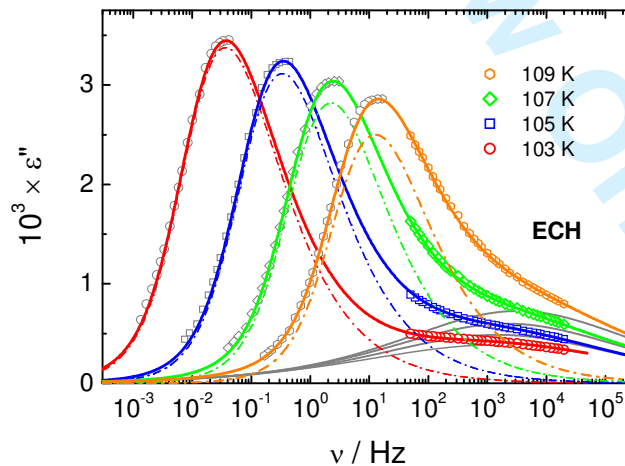


Figure 3. (Color online) Frequency-dependent behaviour of the dielectric loss $\varepsilon''(\nu)$ for supercooled ECH. The spectra are shown as combination of the experimental data at selected temperatures (shown as black open symbols) with the values (gray open symbols) obtained by applying to the master curve the suitable horizontal and vertical shift corresponding to each temperature. Thick solid lines represent the spectra simulated as the sum of a KWW main contribution (dash dot lines) associated with the α -relaxation, and a Cole-Cole contribution (gray lines) corresponding to the β -relaxation.

However a possible limitation of this method is that in the temperature range considered we assume that a large part of the spectra, concerning the α -process, is provided by the master curve while real experimental data are missing and the values of ε''_{\max} and ν_{peak} needed to simulate the spectra were obtained by extrapolation. Moreover the high-frequency tail of the secondary process develops also above the frequency range experimentally accessible. This might introduce some uncertainty for instance on the values of the shape parameters and on the peak frequencies of the primary and secondary processes.

The Havriliak-Negami equation (1) could have been used to describe the main dielectric process, but the corresponding simulated dielectric spectra were narrower than the numerical transform of the KWW function in the peak region closer to the maximum, so the latter function was chosen because it provided a better agreement with the experimental (plus master) data set. It should be pointed out that the value obtained for β_{KWW} with the present approach is compatible with an independent estimate, $\beta_{\text{KWW}} = 0.6 (\pm 0.1)$, obtained using the general correlation [8]

$$m = 250 (\pm 30) - 320 \times \beta_{\text{KWW}} \quad (6)$$

observed for the stretching exponent β_{KWW} and the fragility m [21]

$$m = \left. \frac{d \log_{10} \langle \tau \rangle}{d(T_g/T)} \right|_{T=T_g} \quad (7)$$

which in turn was calculated ($m \cong 56 - 62$) from the VFT parameters for the α -process [22]. Comparable values of m were also deduced independently using thermodynamic data [12, 23].

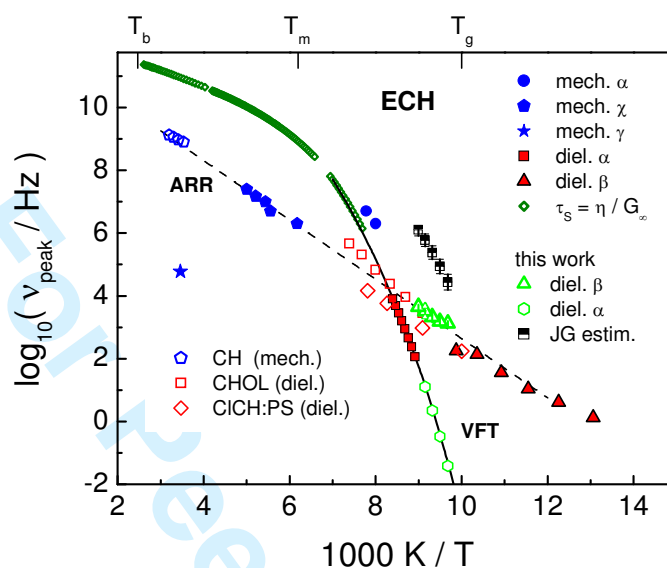


Figure 4. (Color online). Activation plot for the peak frequency ν_{peak} corresponding to the main and secondary dielectric relaxation in ECH. The values corresponding to the relaxational contributions illustrated in fig. 3 are shown as open (green) hexagons (α -process) and open (green) triangles (dielectric β -process). Data concerning the main dielectric peak at higher temperatures and the dielectric β -peak at lower temperatures in glassy ECH are reported from a previous work [1]. The peak frequencies of a possible Johari-Goldstein relaxation estimated on the basis of the coupling model are also shown (half filled squares) for comparison. In the same plot are shown the estimated shear relaxation frequencies [1] and the peak frequencies associated with the mechanical α -, χ - and γ -process [2]. The behaviour of secondary relaxations occurring in cyclohexane (CH) [24], cyclohexanol (CHOL) [25] and dilute solutions of cyclohexyl chloride in polystyrene (ClCH:PS) [26] is closely similar to that of the dielectric β -relaxation observed in supercooled and glassy ECH.

Concerning the secondary process, the present results suggest that it is symmetrically broadened and the strength of the relaxation decreases as the temperature is decreased. This would be in agreement with the general behaviour of the JG relaxation. However a decreasing intensity of the secondary process with decreasing temperature was also observed in the case of a non-JG secondary relaxation associated with the tumbling of the epoxy group [27]. Interestingly, as a result of the present analysis, the peak frequency associated with the secondary relaxation above the glass transition temperature (see the green open triangles in fig. 4 [28]) obeys the same Arrhenius behaviour found at higher temperatures for the secondary mechanical relaxation called the χ -process. Furthermore, this temperature dependence is in good agreement with the behaviour of the dielectric β -peak frequency below the glass transition temperature. In fact, it should be considered that the data below T_g were previously analysed assuming a single relaxational contribution, approximated with a Cole-Cole phenomenological equation. Instead, the high frequency tail of the α -relaxation might still be relevant below T_g , but its effect is hard to estimate because the sub- T_g behaviour of the α -relaxation time, strength, and shape are not known. Taking a contribution from the α -relaxation into account would shift the Cole-Cole peak frequency

of the additional secondary process towards higher frequencies, and a reduced width would be required. Both these effects would tend exactly to improve the agreement between the data points representing the secondary peak frequency below T_g in figure 4 and the data above T_g or at even higher temperatures.

In summary, the present analysis suggests that the peak frequency (or the relaxation time) associated with the dielectric β -relaxation process retains the activated behaviour, with the same activation energy and prefactor, across the glass transition temperature, up to the crossover with the Vogel-Fulcher-Tammann curve associated with the α -peak frequency. According to some studies, the relaxation time of the secondary JG process should become non-Arrhenius above the glass transition temperature [29,30,31,32,33,34]. Since this feature is not satisfied in the present case, the observed behaviour of the dielectric secondary relaxation in ECH would be supportive of a non-JG character, in agreement with the hypothesis of a possible intramolecular origin [1].

On the other hand, the coupling model [35,36] could be adopted in order to estimate the relaxation time τ_β associated with an expected 'true' JG relaxation,

$$\tau_\beta \approx (t_c)^n (\tau_\alpha)^{1-n}, \quad (8)$$

where the parameter t_c (associated with the value 2×10^{-12} s in small molecular liquids [6]) plays the role of the crossover time between cooperative relaxation and independent simple exponential relaxation. The coupling index n relates to the stretching exponent β_{KWW} via $n = 1 - \beta_{\text{KWW}}$. As shown in figure 4, the provisional peak frequency of the intermolecular JG process estimated using the coupling model and the guess β_{KWW} value deduced from the present analysis, is expected to occur at frequencies higher than those at which the secondary contribution has been detected, although the estimated JG peak would become closer to the actual Cole-Cole-like secondary peak on approaching the glass transition temperature. Since the experimental dielectric spectra of glassy ECH, acquired down to 25 K, show no evidence of an additional secondary process faster than the observed β -process, the strength of a true JG relaxation could be too low in the present case, or this process remains insufficiently separated from the β -process to be revealed as an independent feature. Nevertheless, as shown for other small molecular glassformers [37,38], a different approach based for instance on experiments as a function of the applied pressure or experiments on mixtures [39], might allow to detect both the expected JG intermolecular process and the other secondary relaxation, that retains its Arrhenius character even above T_g .

The behaviour of the secondary relaxation as shown in the activation plot of figure 4, along with other evidences provided in ref. 1, suggests that in the case of ethylcyclohexane a secondary relaxation would appear able to 'survive' through the cross-over with the α -relaxation, becoming slower than the α -process at higher temperatures, whereas usually a merging between the α - and the β -relaxation is observed at some (bifurcation) temperature T_β above T_g . [6,40,41]. In many glass-forming liquids the possible existence of such a slow secondary process would be likely hidden by the almost ubiquitous dc conductivity contribution [42,43,18], arising for instance from residual ionic impurities. Moreover it could be surprising that an intramolecular motion, likely responsible for the β -relaxation in ethylcyclohexane, could be seen directly as a dielectric absorption at a frequency lower than that of reorientation of the whole molecule [26]. In fact the χ -process,

that in the activation map appears as corresponding to the *dielectric* β -process, above the crossover region was revealed as a *mechanical* relaxation [2]. Nevertheless a similar situation occurs for another secondary process observed in ethylcyclohexane: the γ -process [2]. The existence of such relaxation slower than the α -relaxation was previously pointed out by means of acoustic attenuation measurements on ethylcyclohexane [44] and on methylcyclohexane [45] at ultrasonic frequencies in the kHz range. The comparison with mechanical measurements on other cyclohexane-derived materials suggested a chair-to-chair conformational transition of the cyclohexane ring as the probable physical origin of the relaxation [1]. A good agreement between the peak frequencies obtained by dielectric and mechanical spectroscopy was observed [1]. Moreover closely similar activation parameters (activation energy and prefactor) characterize relaxation data obtained in the liquid and in the glassy phase [1]. The same discussion seems to fit the behaviour of the mechanical χ -process and of the dielectric β -process in ethylcyclohexane, that for this reason might be understood as a single physical process related to some intramolecular origin. It should be noted that in a previous work on dilute solid solutions of cyclohexane-derived molecules in polymeric matrices [26], two distinct dielectric relaxations were observed in the glassy phase, corresponding to the γ -process and to the χ -process, respectively. While the former process was ascribed to an intramolecular configurational change in the cyclohexyl ring structure as mentioned above, the latter was explained as reorientational tumbling of the whole molecule. This view could explain that different cyclohexyl derivatives show a closely similar Arrhenius behaviour, because of similar structure or molecular volume. However the same picture could not account for the ultrasonic χ -relaxation occurring in the ergodic liquid. Otherwise the correspondence between the low temperature β -relaxation and the high-temperature χ -relaxation should be regarded just as a fortuitous coincidence.

On the basis of the observed features, the possible origin of the χ -relaxation (as well as that of the β -relaxation) could be related to intramolecular modes concerning the cyclohexyl ring. Since a similar relaxation occurs also in pure unsubstituted cyclohexane (see figure 4), its origin could be common to that of the χ -relaxation in ethylcyclohexane and related materials. Transitions between a chair form and more flexible forms like the twist-boat conformation are the only kind of intramolecular reaction that could give rise to isomeric relaxation processes in cyclohexane [46]. However the features of the hypersonic relaxation experimentally observed in cyclohexane [24,47] seem not in agreement with the estimated relaxation time of an equilibrium between the chair and the twist-boat forms [46]. Moreover the χ -relaxation might be explained as a vibrational relaxation process [24], or a relaxation due to translational-vibrational energy transfer [47]. Finally an internal rotation involving only one part of the molecule could be hypothesized, but this possible explanation would need to account for all the different cyclohexane-derived materials (including for instance also unsubstituted cyclohexane and cyclohexanone) whose Arrhenius behaviour corresponds to that of the χ -relaxation. Thus the properties and the nature of this secondary relaxation appear worthy of further investigation.

We would like to remark that recently high resolution dielectric measurements on liquid ethylcyclohexane revealed the existence of a *dielectric* relaxation compatible with the dynamical features of the intramolecular γ -relaxation [1], suggesting that such intramolecular mode could be 'seen' by dielectric spectroscopy although slower than the α -relaxation. It could be very interesting to investigate on the existence of a possible dielectric

signature of the χ -process in the ergodic liquid: this would provide important information to understand the nature of this secondary relaxation.

3. Conclusions

Some unusual features of the dielectric response of supercooled ECH have been analyzed exploiting the scaling properties of the experimental spectra. The results obtained with this approach reconcile the behavior of ECH with the common dynamical properties of glass forming liquids. The main dielectric relaxation can be explained consistently as the superposition of two statistically independent processes: (i) the α -relaxation process, whose temperature independent shape (time-temperature superposition holds) is well accounted for by a KWW response function with a value of β_{KWW} fully compatible with that of other glass forming materials characterized by a similar kinetic fragility; (ii) a β -relaxation, well accounted for by a Cole-Cole equation, whose peak frequency maintains the same Arrhenius temperature dependence also above the glass transition temperature. The latter feature of the β -process would be supportive of a non-JG character of the secondary process, in agreement with a possible intramolecular origin. Moreover, the Arrhenius behaviour of the dielectric β -relaxation in deeply supercooled and glassy ECH closely corresponds to the activated behaviour of the χ -relaxation revealed by mechanical spectroscopy in the same liquid at higher temperatures.

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